Redox and Structural Properties of Transition Metal Dithioacetylacetonates and Related Complexes

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DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results presented have been submitted for publication.

Ian Hamilton Anderson

To my Parents

ACKNOWLEDGEMENTS

I wish to thank Dr. G.A. Heath for his enthusiasm and encouragement throughout these studies. I greatly appreciate the contributions of Dr. M.D. Walkinshaw and Dr. A.J. Blake in solving the respective crystal structures of [Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)] and [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]. In addition, I am very grateful to Dr. D.A. Reed for his DEPT studies of [Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] and [Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2)_2$)] and useful discussions, in conjunction with Dr. I.H. Sadler. I also wish to thank Mr. J.R.A. Miller and Mr. L.H. Bell for recording Nmr spectra, and Mr. M. Grunbaum and Mrs. E. McDougall for performing elemental analyses. I am deeply indebted to the University of Edinburgh for their financial support (Dewar Scholarship) and for the use of facilities. Finally, my thanks to Mrs. M. Bain for typing this thesis.

Abstract

Chapter 1 provides a brief summary of the previously reported electrochemical behaviour of metal bis-dithiochelate complexes (M = Ni, Pd, Pt) and a general outline of the topics discussed in each chapter of this thesis.

Chapter 2 initially describes the preparative routes to the parent systems $[M(S_2C_3RHR')_2]$ and $[M(S_2CNR''_2)_2]$, followed by a detailed account of the syntheses of the hybrid complexes $[M(S_2C_3RHR')(S_2CNR''_2)]$ (M = Ni, Pd, Pt; R, R' = CH_3, Ph, CF_3; R'' = CH_3, C_2H_5, i-C_3H_7, C_4H_9; but not all possible combinations). Infra-red, nmr, electronic and mass spectroscopic studies of these 1,1-dithio-1,3-dithio complexes are also extensively reported.

Chapter 3 is concerned with X-ray crystallographic studies of $[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ and $[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$. These structural results suggest that with the exception of the MS_4 core, the geometric parameters of the (S_2C_3RHR') and $(S_2CNR''_2)$ hybrid moieties are relatively unaltered from those found in the respective parent complexes $[Ni(S_2C_3RHR')_2]$ and $[Ni(S_2CNR''_2)_2]$.

Chapter 4 discusses the voltammetric behaviour of the hybrid systems [M(S_2C_3RHR')($S_2CNR''_2$)], which all display one isolated reversible reduction. Our electrochemical data strongly supports predominant 1,3-dithio-β-diketonate character in the redox-active orbital involved in this reduction.

Chapter 5 describes the syntheses and spectroscopic characterisations of the asymmetrically-substituted systems [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)] (M = Ni,Pd,Pt). Voltammetric investigations, in conjunction with our [M(S_2C_3RHR')($S_2CNR''_2$)]$^{0/1-}$ data, suggest that the two observed one-electron ligand-mediated reductions of the mixed complexes are, at least, consistent with localised electron-acceptance.

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Chapter 1

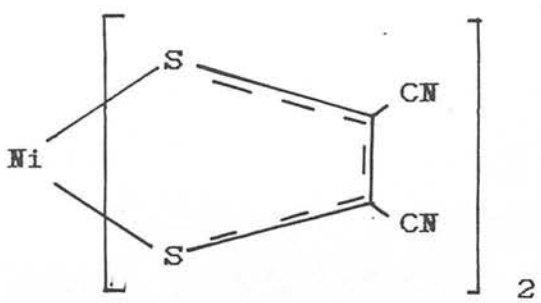
Introduction and Brief Synopsis

Extensive electrochemical studies by Gray, Schrauzer and Holm[1-5], and subsequently summarised by McCleverty[6], have shown that the resonance-stabilised transition metal dithienes, $[M(S_2C_2R_2)_2]$, have a remarkable capacity for sequential ligand-based one-electron uptake, followed by a one-electron reduction involving the metal centre. This redox behaviour is demonstrated below for the sequence of the nickel bis-maleonitrile-dithiolate complex. $[Ni(mnt)_2]$ (I):-

$$[Ni^{II}(mnt)_2]^{0} \rightleftharpoons [Ni^{II}(mnt)_2]^{1-} \rightleftharpoons [Ni^{II}(mnt)_2]^{2-}$$

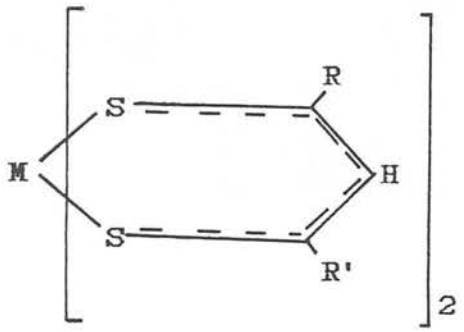
$$\downarrow\uparrow$$

$$[Ni^{I}(mnt)_2]^{3-}$$



(I) $[Ni(mnt)_2] = [Ni(S_2C_2(CN)_2)_2]$

Our general interest in structural variations of such 1,2-dithiochelates has promoted a re-examination of the planar dithio-β-diketonates, $[M(S_2C_3RHR')_2]$ (II), resulting in the recent preparation of many new palladium and platinum complexes through the studies of Joan Leslie[7].

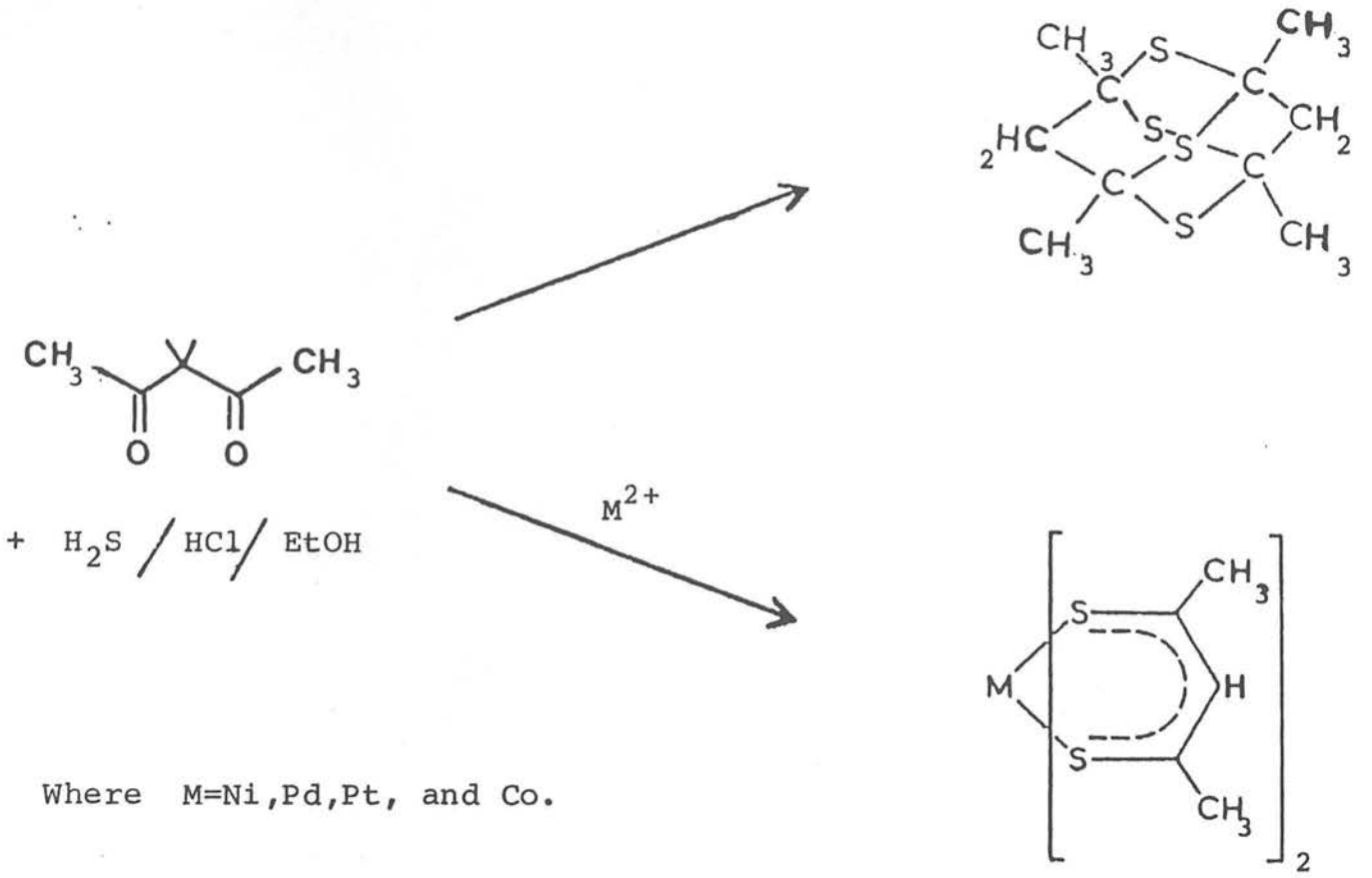


$[M(S_2C_3RHR')_2]$ (II)

The planar monomeric metal 1,3-dithiochelates where R=R'=CH_3, were originally prepared by Martin and Stewart[8] in 1966, by use of a ligand-trapping reaction involving acetylacetone, H_2S and the appropriate metal salt under acidic conditions. This resulted in the production of the complexes $[M(S_2C_3CH_3HCH_3)_2]$, where M = Co, Ni, Pd and Pt, which were assigned the trivial terminology of $M(SacSac)_2$ complexes with SacSac = dithioacetylacetonate (Figure 1.1). The application of the elaborate Martin-Stewart procedure was necessary, as free monomeric dithioacetylacetone (SacSacH) does not exist, preferentially forming a chemically inert tetrathia-adamantane type dimer, $C_{10}H_{16}S_4$.

Extension of this original synthetic principle has resulted in the complexation of other metal centres e.g. M^{III} = Co, Rh or Ir [9] and Fe, Ru or Os [10]. Various alternatively substituted 1,3-β-diketones have also been successfully employed in the synthesis of a wide series of nickel complexes $[Ni(S_2C_3RHR')_2]$, with R,R' = Bu^t, Bu^t; CH_3, Ph; Ph, Ph; CH_3, CF_3 and CF_3, Ph [11-13]. The corresponding palladium and platinum systems, which have

Figure 1.1 - The Synthesis of $M(SacSac)_2$ (R.L. Martin and I.M. Stewart, Nature,1966,210,522.)



Where M=Ni,Pd,Pt, and Co.

been previously mentioned[7], were produced and characterised in this laboratory.

Two early and contrasting predictions were made concerning the possible redox behaviour of the metal bis-dithio-β-diketonates. McCleverty suggested that the $[M(S_2C_3RHR')_2]$ systems would exhibit similar ligand-based electron-transfer processes to those observed in the dithienes $[M(S_2C_2R_2)_2]$. This postulate was contradicted by Schrauzer,[14] who emphasised the topological distinction between 'even' (1,2-dithio) and 'odd' (1,1-dithio and 1,3-dithio) resonance-stabilised ligands and suggested that well-defined reduction steps like those associated with the dithiene complexes would not be discovered in the 'odd' systems. Early molecular orbital calculations appeared to strengthen Schrauzer's claim that the 'odd' systems would reveal only metal-based cathodic behaviour, by identifying the nature of the lowest acceptor orbitals in both the (1,1-dithio) and (1,3-dithio) ligands as significantly antibonding.

Nevertheless, intial polarographic investigations into planar dithio-β-diketonates'[5] in acetone, consistently displayed two successive one-electron reductions. The first reduction of $[Co(S_2C_3CH_3HCH_3)_2]$ was relatively easy and designated a Co^{II}/Co^{I} transition. The cathodic behaviour of the d^8-triad complexes (whether metal or ligand-based) was uncertain until the E° potentials obtained for a series of $[Ni(S_2C_3RHR')_2]$

systems were shown to be strongly dependent upon the Hammett substituent parameters of R and R' [16,17].

Heath and Leslie[18] provided further evidence that both reductions of the dithio-β-diketonates of Ni, Pd and Pt were ligand-based. The E° values changed little on changing the metal centre from nickel through to platinum, for constant R, R'. Moreover, a roughly parallel linear dependence of E° versus substituent inductive parameters existed for $[Ni(S_2C_3RHR')_2]$ and $[Ni(S_2C_2RR')_2]$ systems, strongly supporting the view that in both cases these reductions result in essentially ligand-based radical anions. Therefore the two reductions observed in the d^8-(1,3-dithio) complexes are considered to be:-

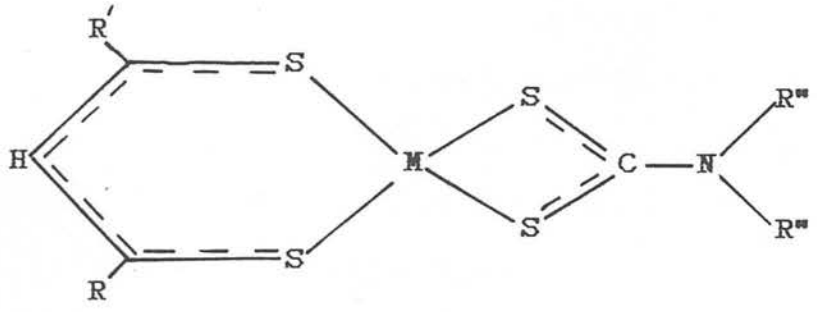
$$[M^{II}(S_2C_3RHR')_2]^{\cdot} \rightleftharpoons [M^{II}(S_2C_3RHR')_2]^{1-} \rightleftharpoons [M^{II}(S_2C_3RHR')_2]^{2-}$$

In contrast to the resonance-stabilised (1,2-dithio) and (1,3-dithio) complexes, resonance-stabilised 1,1-dithiochelates such as $[M(S_2CNR''_2)_2]$ have been shown via esr studies to accept an electron only at more negative potentials with the reduction of the metal centre[19], thus conforming to the 'odd' ligand criterion of Schrauzer.

$$[M^{II}(S_2CNR''_2)_2]^{\cdot} \rightleftharpoons [M^{I}(S_2CN\ R''_2)_2]^{1-}$$

We have now prepared and characterised (Chapter 2) a range of hybrid (1,1-dithio)(1,3-dithio) complexes of the

type [M(S_2C_3RHR')($S_2CNR''_2$)] (III), where M = Ni, Pd and Pt, which make an interesting contrast with the 'isomeric' bis-(1,2-dithiene) systems.



(III) [M(S_2C_3RHR')($S_2CNR''_2$)]

These resonance-stabilised hybrids once again conflict with Schrauzers 'odd-even' distinction by revealing cathodic behaviour that corresponds to an isolated one-electron reduction of the single (S_2C_3RHR') ligand. This takes place at more negative potentials than observed in the corresponding parent bis-1,3-dithio complex, [M(S_2C_3RHR')$_2$]$^{0/1-}$ (Chapter 4).

The reinforcement of mutually complementary π-acceptor (S_2C_3RHR') and π-donor (S_2CNR_2) ligands lead to the hybrid systems gaining additional overall stability. X-ray structural studies show that the MS_4 cores of these momomeric composite complexes though strongly non-square, are still strictly planar.

In addition to answering many questions regarding electronic structural and electrochemical properties of the SacSac ligand in isolation, these hybrid products also demonstrate the ability of the dithio-β-diketonate ligands to readily participate in ligand-scrambling

processes. Such interesting transformations have been largely neglected in the case of 1,3-dithiochelates, in contrast to 1,1-dithio- and 1,2-dithiochelates. Various reactions between these smaller ring systems have provided numerous examples of composite (1,1-dithio)(1,1-dithio) complexes [20-21], hybrid (1,1-dithio)(1,2-dithio) systems[21-24] and mixed (1,2-dithio)(1,2-dithio) complexes[25]. $[M(S_2C_3RHR')(S_2CNR''_2)]$ systems represent the first observed class of (1,1-dithio)(1,3-dithio) hybrids, thus supplementing the asymmetric (1,3-dithio)(1,2-dithio) compound, $[Bu_4N][Ni(S_2C_3CH_3HCH_3)(S_2C_2(CN)_2)]$, reported by Hendrickson, Hope and Martin[16].

Although the voltammetric investigations into the dithio-β-diketonates reveal two ligand-based single-electron reductions, it is not possible to determine in the parent systems $[M(S_2C_3RHR')_2]$ whether the electrons involved in the successive redox steps enter acceptor orbitals delocalised over the whole molecule, as previously suggested by Bond and co-workers[15], or, alternatively are each situated in a localised orbital associated exclusively with an individual 1,3-dithio-chelate ring. We therefore examined this problem via the preparation, characterisation and reduction of the first asymmetrically-substituted bis (1,3-dithio) systems $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$, where M = Ni, Pd, Pt. Our observations on the limited extent of electronic inter-

ligand communication in these planar bis-1,3-dithio complexes are reported in Chapter 5.

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Chapter 2 - The Synthesis and Characterisation of Nickel, Palladium and Platinum Organo-Sulphur Ring Complexes

i) $[M(S_2C_3RHR')_2]$

ii) $[M(S_2CNR"_2)_2]$

iii) $[M(S_2C_3RHR')(S_2CNR"_2)]$

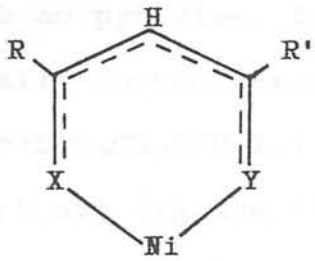
2.1 Introduction to [M(S$_2$C$_3$RHR')$_2$] Systems

Although the chemical and structural properties of metal 1,1-dithiochelates [1-3] and 1,2-dithiochelates [4,5] have been extensively compiled, similar attention has not been devoted to metal 1,3-dithio-β-diketonates, despite their initial synthesis twenty years ago by Martin and Stewart. Only one informative review of metal 1,3-dithio-β-diketonates has appeared, prepared by Lockyer and Martin[6] in 1980. This identifies the relevant physical properties and reactions so far discovered in the systems [M^n(S$_2$C$_3$RHR')$_n$] with particular emphasis, M = Fe, Ru, Os, Co, Rh, Ir, Ni, Zn.

The substitution of oxygen by sulphur in the monothio- and dithio- metal complexes effectively prevents polymerisaiton, in comparison to its common occurence in the divalent first row transition-metal diketonates. Nickel(II), zinc(II) and cobalt(II) 1,3-β-diketonates exist in trimeric [7,8] (Ni, Zn) and tetrameric [9,10] (Co) geometric forms in the solid state. By contrast, [Pd(O$_2$C$_3$CH$_3$HCH$_3$)$_2$] and [Pt(O$_2$C$_3$CH$_3$HCH$_3$)$_2$] are both planar monomeric species [11], due to the large ligand field stabilisation energies associated with the second and third row metals which stabilise the planar d^8 form. Clearly the associated LFSE exerts a greater influence than the factor of co-ordinative saturation, dominant in [Ni(O$_2$C$_3$CH$_3$HCH$_3$)$_2$] and other first-row metal 1,3-β-diketonates. Inhibition of oligomerisation by thio-

substitution in the first row metal complexes is amply demonstrated by the observation that the variously substituted NiS_2O_2, NiS_3O and NiS_4 systems are without exception planar, monomeric compounds.

Gerlach and Holm [12,13] further investigated the stereochemical consequences of replacing O by S in the series of structurally related chelates:-



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1) X=Y=O; β-diketone, 2) X=O, Y=S; monothio-β-diketone, 3) X=O, Y=NR; β-ketoamine, 4) X=S, Y=NR; β-aminothione

The β-ketoamines (3) and β-aminothiones (4) proved to be useful in illustrating that sulphur-ligated metal complexes of nickel(II) prefer (compared to O-ligated analogues) to exist in square-planar configurations, as previously discussed for the NiS_2O_2, to NiS_4 systems. Nickel β-ketoamines and β-aminothiones both display tetrahedral$\rightleftharpoons$planar equilibria in non-co-ordinating solvents (chloroform and carbon tetrachloride). The proportion of the planar isomer is greater in the β-aminothione nickel compounds than that observed in the corresponding nickel β-ketoamines, once again reinforcing

the tendency for sulphur to stabilize the planar form of monomeric complexes.

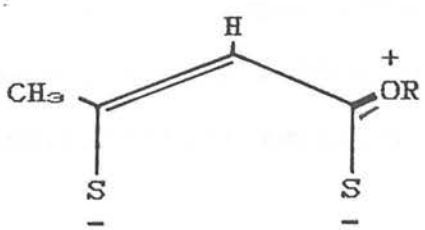
The chemistry of metal "SacSac" complexes i.e. their reactions once prepared, is largely unresearched. Investigations into possible ligand substitution processes of metal 1,3-dithio-β-diketonates have, until recently, been largely limited to three topics:

i) The refusal of $[Ni(S_2C_3CH_3HCH_3)_2]$ to react with Lewis bases such as pyridine, to yield the anticipated axially co-ordinated adducts [14,15].

ii) Reactions of $[M^n(S_2C_3CH_3HCH_3)_n]$ complexes with nitrosyl and carbonyl ligands [17-19], to form complexes such as $[Co(S_2C_3CH_3HCH_3)_2(NO)]$ and $[Fe(S_2C_3CH_3HCH_3)_2(NO)_2]$.

iii) Ligand-scrambling reactions between parent $[Ni(S_2C_3ORHCH_3)_2]$ and $[Ni(S_2C_3NR_2HCH_3)_2]$ systems to yield mixed-ligand nickel bis-1,3-dithio-β-diketonate complexes $[Ni(S_2C_3ORHCH_3)(S_2C_3NR_2HCH_3)]$ [16].

These -'OR' substituted derivatives are a subset of our own electrochemically studied $[M(S_2C_3RHR')_2]$ systems (M=Ni, Pd, Pt; R, R'=Bu^t, CH_3, Ph or CF_3) with substantial contribution from the canonical form,



and therefore are not characteristic of all metal bis-1,3-dithio-β-diketoneates.

Recently, these areas of investigation have been augmented by the preparation and study of catalytically active nickel complexes, containing 1,3-dithio-β-diketonate ligands of the general type $[Ni(S_2C_3RHR')(PR_3")Cl]$ ($R=R'=CH_3$; $R=CH_3$, $R'=CF_3$; $R"$ = C_2H_5, C_3H_7, C_6H_5) [20]. These square-planar sixteen-electron systems are currently being extensively examined with respect to their ability to function as effective oligomerisation and double-bond shift isomerisation catalysts under mild conditions, when activated with an alkylaluminium co-catalyst. Initial results reveal that the catalytic activity is dependent upon the particular 1,3-dithio-β-diketone, the phosphine and the temperature.

Cavell, Masters et. al. have completed X-ray structural determinations of $[Ni(S_2C_3CH_3(CH_2CH=CH_2)CH_3)Cl(P(C_2H_5)_3)]$ [21] and $[Ni(S_2C_3CH_3HCH_3)Cl(P(C_4H_9)_3)]$ [22], in order to correlate geometric parameters with those discovered in $[Ni(S_2C_3CH_3HCH_3)Cl(P(C_2H_5)_3)]$ prepared and studied by Fackler and Masters[23] in 1979. Interestingly, this complex exhibited fluxional proton nmr behaviour, with the two methyl resonances displaying magnetic inequivalence only at low temperatures, parallel to the fluxionality observed in the analogous 1,1-dithio-complexes $[M(S_2CNR_2)X(PR'_3)]$ ($M=Ni,Pd$; $R=C(CH_3)_3$, C_2H_5).

Therefore the range of known reactions open to metal 1,3-dithio-β-diketonates is significantly extended by our preparation of numerous hybrid complexes, $[M(S_2C_3RHR')(S_2CNR''_2)]$ (M=Ni,Pd,Pt; R,R'=CH_3,Ph or CF_3; R''=CH_3, C_2H_5, i-C_3H_7 or C_4H_9). This establishes the wide-spread ability of the parent bis-1,3-dithio systems to participate in scrambling processes in non-co-ordinating media, such that 1,3-dithio-ligands are transferred without degradation from one metal ion to another, as discussed below and in Chapter 5.

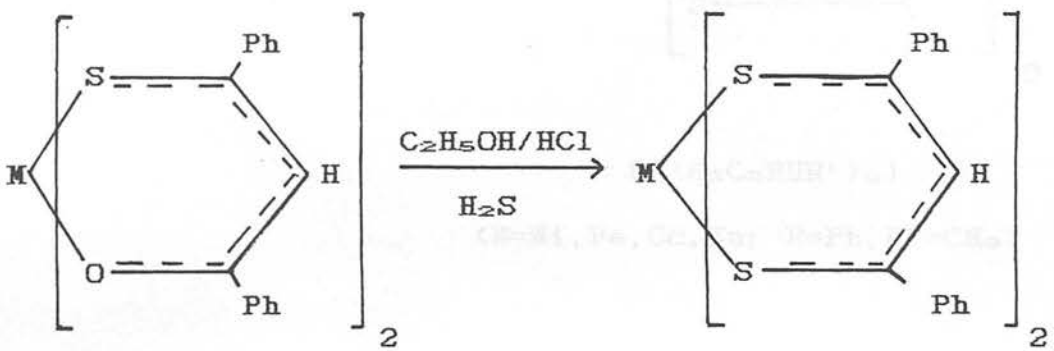
2.2 Synthesis and Characterisation of $[M(S_2C_3RHR')_2]$ Systems

a) Possible Preparative Routes

The Martin-Stewart metal-trapping process (Figure 1.1) remains the major preparative route in this study to synthesise metal bis-1,3-dithio-β-diketonate complexes, although three further possible synthetic schemes can be considered. The complexes of the nickel triad, $[M(S_2C_3RHR')_2]$ (M=Ni,Pd,Pt), where R,R'=t-Bu, Ph,CF_3 and CH_3 (but not all possible combinations) were successfully obtained by the general Martin-Stewart procedure except that the syntheses were carried out at 203K, rather than ambient temperatures as originally used in the preparation of the $[M(S_2C_3CH_3HCH_3)_2]$ complexes (which were assigned the trivial terminology of $[M(SacSac)_2]$ by Martin and Stewart).

Method 2

Monothio-β-diketones, $R(CO)CH_2(CS)R'$, can be readily prepared and isolated as stable solids or oils, which can subsequently be deprotonated in combination with relevant metal ions, to yield the corresponding complex $[M(SOC_3RHR')_2]$ [25,26] Treatment of this monothio-complex with H_2S in an ethanolic HCl medium yields the fully sulphurated MS_4 compound. This procedure is particularly helpful in preparing dithio- derivatives with bulky R/R' substituents, for example in considering the dithio-analogue of dibenzoylmethane, where the MS_4 product is obtained in much greater yield for $[M(SOC_3PhHPh)_2]$ than in a direct Martin-Stewart operation.

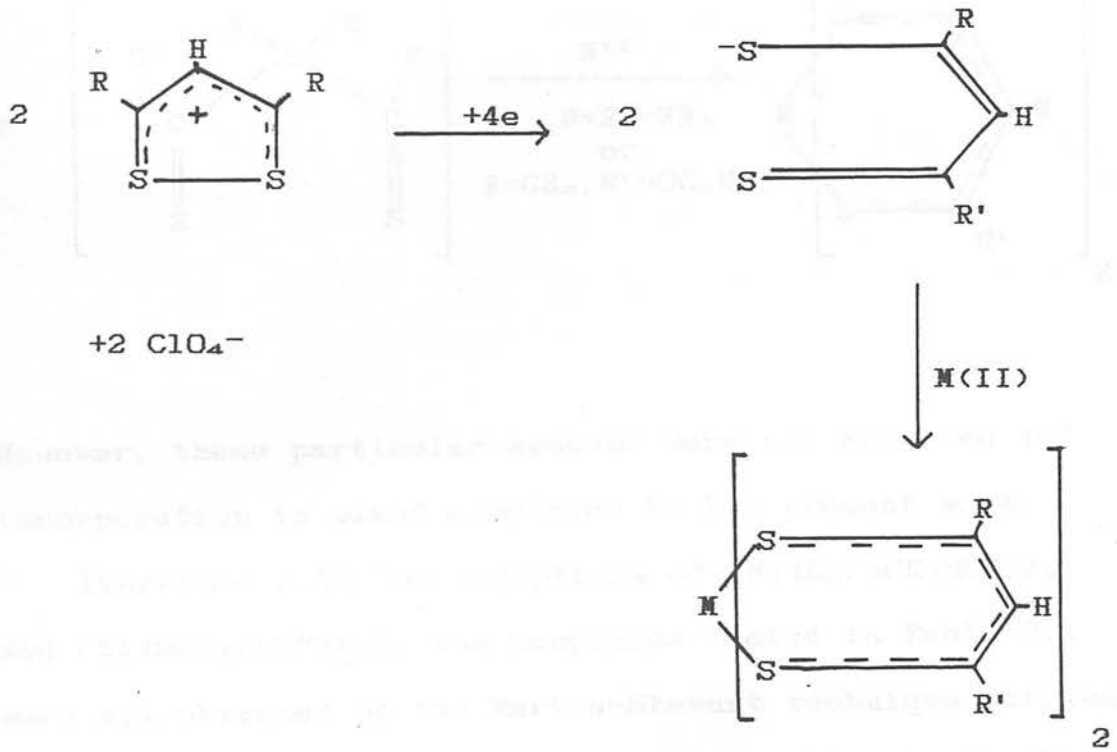


$[M(SOC_3PhHPh)_2]$ $[M(S_2C_3PhHPh)_2]$

Method 3

This route was not explored here but involves the reduction of a 1,2-dithiolium cation with Na BH_4 to yield directly the required ligand [27]. The presence of the appropriate metal ion in the mixture enables the formation of the desired metal bis-1,3-dithio-β-

diketonate complex to proceed immediately, before the thermally unstable free ligand decomposes.



$[M(S_2C_3RHR')_2]$

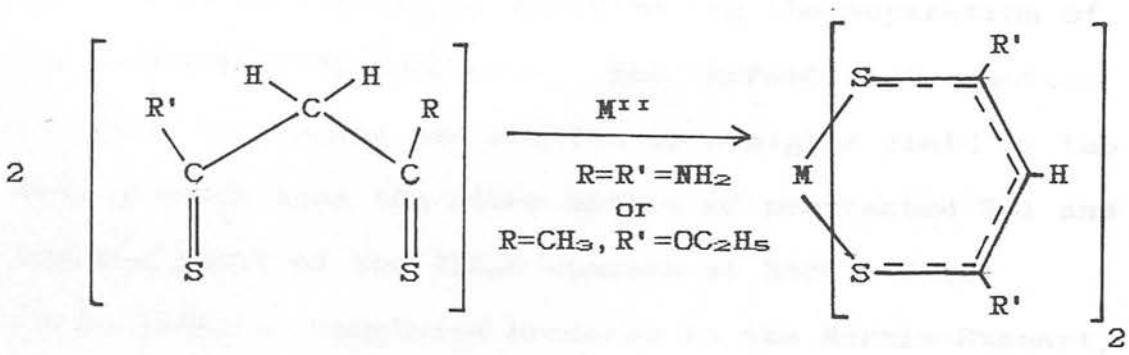
(M=Ni, Fe, Co, Zn; R=Ph, R'=CH_3)

The dithiolium salts are separately available by literature methods[28].

Method 4

This synthetic pathway was not investigated as it is limited to the production of $[M(S_2C_3ORHCH_3)_2]$ (R=C_2H_5) [29] and $[M(S_2C_3NH_2HNH_2)_2]$ [30,31] complexes. Here, unusually, the free ligands are available (resistant to polymerisation) and the complexes are obtained through

the direct 2:1 interaction of the free 1,3-dithio-β-diketonate ligand with the appropriate metal (II) salt:-



However, these particular systems were not required for incorporation in mixed complexes in the present work.

Therefore with the exceptions of $[Ni(S_2C_3CH_3HCH_3)_2]$ and $[Ni(S_2C_3PhHPh)_2]$, the complexes listed in Table 2.1 were all obtained by the Martin-Stewart technique carried out at 203K. For $[Ni(S_2C_3CH_3HCH_3)_2]$ itself, the Martin-Stewart procedure at ambient temperatures mainly produces the intermediate product $[Ni(S_2C_3CH_3HCH_3)(SOC_3CH_3HCH_3)]$, rather than the required symmetric planar NiS_4 complex. In order to convert this mixed ligand product to the desired $[Ni(S_2C_3CH_3HCH_3)_2]$ complex, the following reaction devised by Blejean[32] was carried out.

Reaction 2.1

$$2[Ni(S_2C_3CH_3HCH_3)(SOC_3CH_3HCH_3)] \xrightarrow[HBr\,(trace)]{CH_3CN,\ 80°C,\ 3hrs} [Ni(S_2C_3CH_3HCH_3)_2]\downarrow + [Ni(SOC_3CH_3HCH_3)_2]$$

Fortunately, the bis-SO complex is relatively soluble in acetonitrile, facilitating the separation of the insoluble $[Ni(SacSac)_2]$. The 'scrambling' reaction in CH_3CN is cleaner and results in a higher yield of the NiS_4 product than the older method of protracted HCl and H_2S treatment of the NiS_3O species at 323K. Other $[M(S_2C_3RHR')_2]$ complexes produced by the Martin-Stewart method tend not to 'stick' at the NiS_3O stage.

The general implication that β-dithio-ligands can be exchanged between metal centres without degradation in such ligand-scrambling processes, as that discovered by Blejean, is vital for this thesis.

(b) Experimental

Suitable starting materials were $NiCl_2.6H_2O$ and $M(PhCN)_2Cl_2$ (M=Pd,Pt), rather than the corresponding palladium or platinum chlorides, because of the enhanced solubility of bis-benzonitrile salts in ethanol and the additional factor that PhCN is a superior leaving group. Dry ethanol was prepared by refluxing over magnesium turnings, with a few crystals of iodine added, followed by distillation immediately prior to use. HCl was generated by dropping concentrated sulphuric acid onto concentrated hydrochoric acid with vigorous stirring. The resultant HCl gas was dried by bubbling through concentrated H_2SO_4. H_2S was generated via a modified Kipps apparatus, by dropping a 1:1 concentrated HCl:

water mixture onto ferrous sulphide sticks. The H_2S produced was dried by passage through three anhydrous $CaCl_2$ towers. The appropriate β-diketonate ligands were obtained commercially and used without further purification.

A typical low temperature synthesis (203K) is outlined below for $[Pd(S_2C_3CH_3HCH_3)_2]$. $Pd(PhCN)_2Cl_2$(0.20g) was dissolved in dry ethanol (10 ml) containing excess acetylacetone (1.5 ml). The system was then cooled to 203K and flushed with nitrogen for a period of five minutes. HCl was conveyed through the system for twenty minutes. H_2S was then passed for forty-five minutes via a fritted bubbler, whilst maintaining a small positive pressure of nitrogen throughout.

The resultant solution was allowed to slowly revert to room temperature and stand for twenty-four hours under N_2, to yield a bright-red precipitate, which was collected via filtration and washed with ethanol. The $[Pd(S_2C_3CH_3HCH_3)_2]$ complex was then recrystallised from a 2:1 mixture of methanol: methylene chloride (as were all other $[M(S_2C_3RHR')_2]$ complexes), to produce 0.125g of $[Pd(S_2C_3CH_3HCH_3)_2]$ (65%).

The $[M(S_2C_3RHR')_2]$ compounds are all intensely coloured and generally of limited solubility in CH_2Cl_2 (best), $CHCl_3$, CH_3COCH_3, $C_6H_5CH_3$ and C_6H_6, but essentially insoluble in other organic solvents such as alcohols, alkanes and ethers. The complexes, prepared

and recrystallised as described, are found to be analytically pure and non-conducting in a range of organic solvents. The [M(S_2C_3RHR')$_2$] systems were characterised by i.r., uv/vis and mass spectroscopic techniques, involving direct comparisons with established results. Tabulation of the spectroscopic parameters of the [M(S_2C_3RHR')$_2$] 'parent' complexes is deferred to Tables 2.3-2.6, where they are compared with those obtained for the hybrid systems [M(S_2C_3RHR')($S_2CNR''_2$)].

Elemental analyses and mass spectroscopic data are shown in Table 2.1. Mass spectra of the [M(S_2C_3RHR')$_2$] complexes all exhibit a medium-intensity parent ion $[ML_2]^{+\cdot}$ signal, and a stronger dithiolium ion $[L^+]$ signal, which invariably dominates the spectrum, along with its characteristic fragmentation pattern[33].

2.3 Preparation and Properties of [M($S_2CNR''_2$)$_2$] Complexes; M=Ni,Pd,Pt

Nickel bis-dialkyldithiocarbamates were initially reported by Delepine in 1908[34], when he discussed [Ni($S_2CN(^iBu)_2$)$_2$] and [Ni($S_2CN(H)_2$)$_2$], having earlier examined [Pt($S_2CN(^iBu)_2$)$_2$][35]. Systematic investigations into a series of nickel bis-N,N-dialkyl-dithiocarbamates were not completed until 1924, through the studies of Whitby and Matheson[36]. Palladium and platinum bis-dialkyl-dithiocarbamates have largely been studied and

Table 2.1 - $[M(S_2C_3RHR')_2]$ Complexes - Analytical and Mass Spectroscopic Data

Complex	Yield	Elemental Analysis				Mass Spectrum (m/e Values)	
		Expected		Observed		$[M(S_2C_3RHR')_2]^{+\cdot}$	$(S_2C_3RHR')^+$
		%C	%H	%C	%H	Parent	Dithiolium Ion
$Ni(S_2C_3CH_3HCH_3)_2$	60%	37.4	4.4	37.2	4.4	320	131
$Ni(S_2C_3PhHCH_3)_2$	35%	53.9	4.0	53.7	4.2	444	193
$Ni(S_2C_3PhHPh)_2$	10%	63.3	3.9	59.8	3.95	568	255
$Ni(S_2C_3CF_3HCH_3)_2$	40%	28.0	1.9	27.7	2.1	428	185
$Ni(S_2C_3CF_3HPh)_2$	25%	43.4	2.2	43.2	2.2	552	247
$Pd(S_2C_3CH_3HCH_3)_2$	65%	32.6	3.8	32.9	3.8	368*	131
$Pd(S_2C_3CF_3HCH_3)_2$	50%	25.3	1.7	25.4	1.8	476*	185
$Pt(S_2C_3CH_3HCH_3)_2$	60%	26.3	3.1	26.0	3.1	457†	131
$Pt(S_2C_3CF_3HCH_3)_2$	20%	21.2	1.4	21.0	1.5	565†	185

* ^{106}Pd † ^{195}Pt

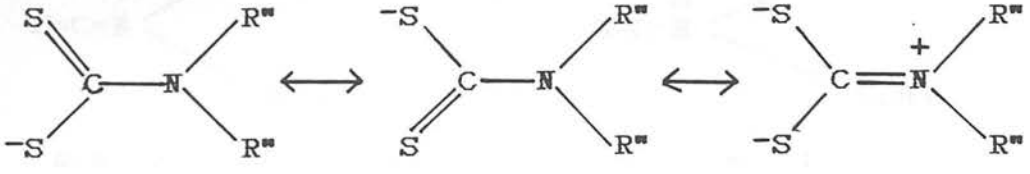
crystallographically characterised by Amanov et.al.[37] and Beurskens et.al.[38].

Two basic preparative methods were used to obtain the metal bis-dialkyl-dithiocarbamato complexes in the course of this present study. For $[M(S_2CNR''_2)_2]$ complexes where $R''=CH_3$ or C_2H_5, the metal bis-dithiochelates were prepared via the direct 2:1 molar interaction of an aqueous solution of the commercially available sodium dialkyldithiocarbamate salt, $Na.S_2CNR''_2$, with an aqueous solution containing the required metal ion. $NiCl_2.6H_2O$ was used as a source of nickel ions with K_2PtCl_4 and $PdCl_2$ providing Pt(II) and Pd(II) ions. The aqueous insoluble complexes were then collected and recrystallised from chloroform, with the exception of the dimethyl substituted complexes which are virtually insoluble in all solvents.

Nickel bis-N,N-di-isopropyldithiocarbamate, $[Ni(S_2CN(i\text{-}C_3H_7)_2)_2]$, and platinum bis-N,N-di-isobutyl-dithiocarbamate, $[Pt(S_2CN(i\text{-}C_4H_9)_2)_2]$, were both synthesised by a modified Whitby and Matheson procedure, initially pursued by Cavell and Sugden[39]. This method essentially involved the synthesis of the sodium dialkyl-dithiocarbamate salt in solution, followed by direct introduction of the relevant transition metal ion, to form the target complex. The first step of the preparation concerned the mixing of CS_2 (0.05 moles) with an aqueous solution of 20% KOH (0.05 moles), followed by the slow dropwise addition of the requisite secondary

amine ((i-C_4H_9)$_2$NH or (i-C_3H_7)$_2$NH, 0.05 moles), whilst cooling and constantly agitating the reacting system. The resulting solution was then gradually allowed to combine with an aqueous mixture containing sodium acetate (0.15 moles) and $NiCl_2.6H_2O$ or K_2PtCl_4 (0.05 moles), as required. The precipitated complexes were then collected and recrystallised from chloroform.

In organic media, the relative solubilities of the metal bis-N,N-dialkyldithiocarbamato complexes improve as the magnitude of the alkyl chain is increased. Infra-red spectroscopy is extremely useful in studying [M(S_2CNR"$_2$)$_2$] systems, with the ν(C-N) vibration of the S_2C-NR"$_2$ bond between 1550-1480cm^{-1} receiving particular attention. This section of the spectrum has been labelled the "thioureide" vibrational region by Randle[40] and further shown by Chatt[41] to demonstrate the important role played by canonical form (3) in [M(S_2CNR"$_2$)$_2$] complexes:

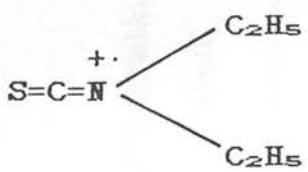


(1) (2) (3)

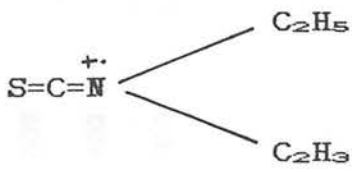
As ν(C-N) for these dithiochelates lies at intermediate frequency to the vibrational regions assigned to ν(C-N) single bonds (1350-1250cm^{-1}) and ν(C=N) (1690-1630cm^{-1}), it can best be explained as a

vibration of a $C=N^{+}<$ species. Variation in the alkyl chain also affects the relative position of the $\nu(C-N)$ band ($R''=CH_3=1535cm^{-1}$, $C_2H_5=1515cm^{-1}$, $C_3H_7=1485cm^{-1}$). The longer the alkyl chain, the lower the frequency associated with the thioureide vibration. The i.r. spectra of corresponding Ni, Pd and Pt systems are almost identical throughout the spectral range.

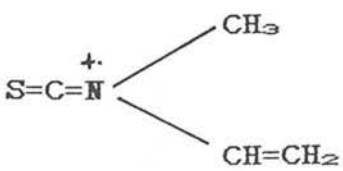
Proton nmr data shows very slight changes on moving from Ni to Pt centres with constant R'' substituents. Equally for constant metal centres and differing R'' groups (e.g. C_2H_5, $i\text{-}C_3H_7$; M=Ni), the electronic spectra are almost identical. Mass spectra of metal bis-N,N-dialkyldithiocarbamato-complexes are dominated by intense parent ion m/e signals and by fragmentation through a series of isothiocyanate ions. Some possible assignments for the most frequently encountered isothiocyanate m/e signals (Table 2.2) are as follows:



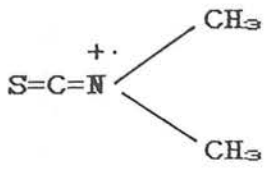
m/e 116



m/e 102



m/e 100



m/e 88

Table 2.2 - $[M(S_2CN(R''_2)_2]$ Complexes - Elemental Analyses and Mass Spectroscopic Data

Complex	Recrystallised Yield	Elemental Analysis						Mass Spectrum	
		Expected			Obtained			Parent	Isothiocyante Ions
		%C	%N	%H	%C	%N	%H		
$[Ni(S_2CN(CH_3)_2)_2]$	100%(a)	24.1	9.4	4.0	24.1	9.2	4.1	298	88
$[Ni(S_2CN(C_2H_5)_2)_2]$	85%	33.8	7.9	5.7	33.7	8.1	5.4	354	116,88
$[Ni(S_2CN(C_3H_7)_2)_2]$	65%	40.9	6.8	6.9	40.7	6.9	6.9	410	102,100
$[Pd(S_2CN(C_2H_5)_2)_2]$	80%	29.8	7.0	5.0	29.3	6.4	5.2	402	116,88
$[Pt(S_2CN(C_2H_5)_2)_2]$	80%	24.4	5.7	4.1	24.7	5.9	4.1	491	116,88
$[Pt(S_2CN(C_4H_9)_2)_2]$	55%	35.8	4.6	6.0	36.2	4.6	6.1	603	(b)

Notes

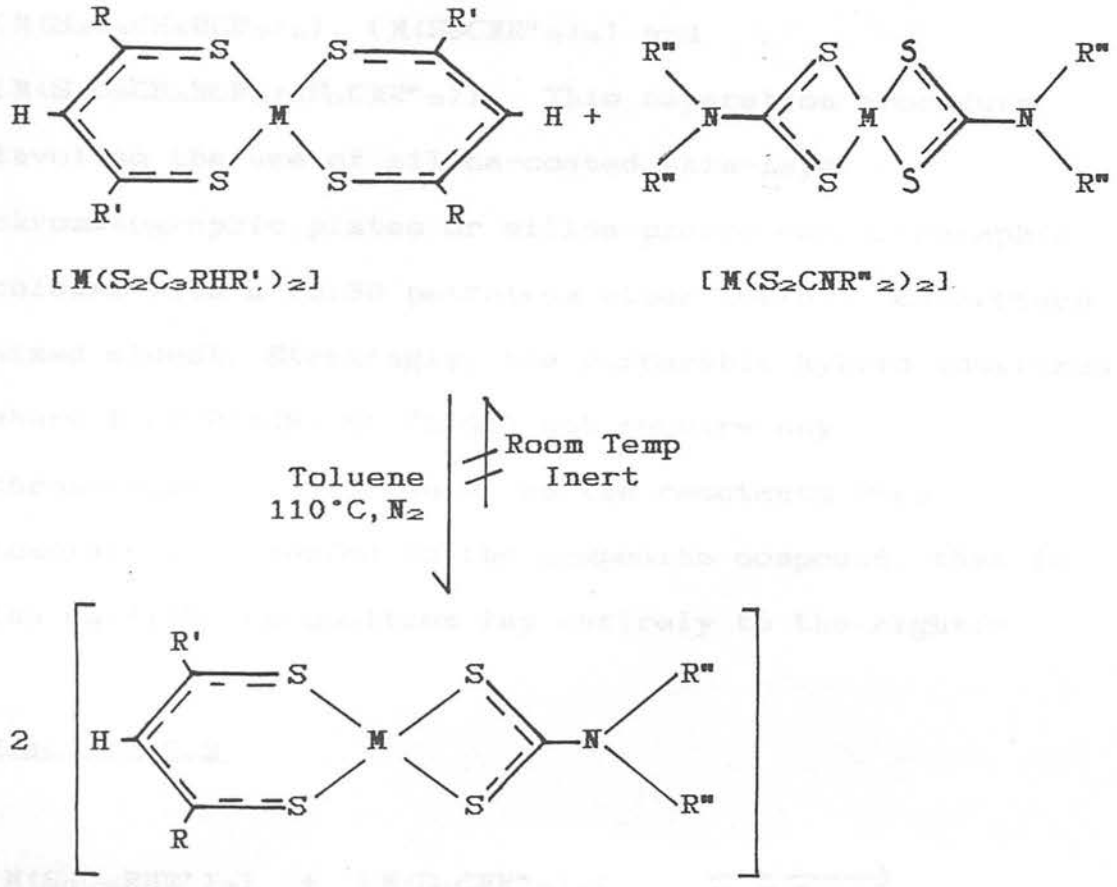
(a) System not recrystallised due to its unsolubility

(b) Mass Spectrum very complex in nature in the isocyanate ion region

2.4 Syntheses of [M(S$_2$C$_3$RHR')(S$_2$CNR"$_2$)] Hybrid Complexes

The basic preparative route to these hybrid complexes is shown in Scheme 2.1 below.

Scheme 2.1



Equimolar amounts of the appropriate starting materials were heated in toluene (e.g. 0.2 mmole of each complex in 50 ml), under a nitrogen atmosphere. The reaction time was dependent upon the metal centre and the alkyl substituents (R and R') of the 1,3-dithio-β-diketonate ligand. The reaction times varied between 10 and 90 hours. All hybrid complexes are stable

during the purification or isolation procedures, conducted at room temperature, and outlined below.

In the preparation of the hybrid systems where R=R'=CH_3, the reaction mixture requires chromatographic treatment in order to separate the three constituents, $[M(S_2C_3CH_3HCH_3)_2]$, $[M(S_2CNR''_2)_2]$ and $[M(S_2C_3CH_3HCH_3)(S_2CNR''_2)]$. This separation procedure involved the use of silica-coated thin-layer chromatographic plates or silica-packed chromatographic columns with a 70:30 petroleum ether (60/80): chloroform mixed eluent. Strikingly, the comparable hybrid complexes where R or R'=CF_3 or Ph did not require any chromatographic procedure, as the reactants were completely converted to the composite compound, that is the equilibrium position lay entirely to the right:-

Reaction 2.2

$$[M(S_2C_3RHR')_2] + [M(S_2CNR''_2)_2] \rightleftharpoons 2[M(S_2C_3RHR')(S_2CNR''_2)]$$

This alteration in the equilibrium distribution resulting from the introduction of electron-withdrawing substituents (R or R'=CF_3, Ph) is further discussed in section 2.5.

Mass spectroscopic studies for the hybrids reveal two major signals in every case, corresponding to the parent ion $[MLL']^+$ and the dithiolium ion $(S_2C_3RHR')^+$,

derived from the 1,3-dithio-β-diketonate ligand, with the dithiolium ion m/e trace slightly more intense. The detection of isothiocyanate m/e signals are hindered by strong m/e traces arising from the further fragmentation of the dithiolium ion in the m/e region below 120.

Since these $[M(S_2CNR''_2)(S_2C_3RHR')]$ species are all new compounds and represent a new category of complex, the particular experimental methods used to obtain each specific complex are reported in detail below.

[(dithio-acetylacetonato)(N,N-dimethyldithiocarbamato)nickel(II)]

$[Ni(S_2C_3CH_3HCH_3)(S_2CN(CH_3)_2)]$ $NiC_8H_{13}S_4N$

$[Ni(S_2CN(CH_3)_2)]$ (0.040g, 0.13mmole) and $[Ni(S_2C_3CH_3HCH_3)_2]$ (0.043g, 0.13mmole) were dissolved in nitrogen-flushed toluene (40ml). The resulting solution was then slowly stirred and the passage of N_2 maintained whilst the system was heated to 110°C for a period of twenty hours. The solvent was then removed to produce an air-stable wine-coloured solid. The hybrid product was isolated from the two reactants using a silica-packed chromatographic column and a mixed eluent of 60/80 petroleum ether: chloroform (70:30). The hybrid species, $[Ni(S_2CN(CH_3)_2)(S_2C_3CH_3HCH_3)]$, is notably more soluble than the parent $[Ni(S_2CN(CH_3)_2)_2]$ and was recrystallised from a dichloromethane: 60/80 petroleum ether mixture in air.

Equilibrium yield=75%, Recrystallised yield: 0.063g(75%)

Mass spectrum: m/e 309[$Ni(S_2C_3CH_3HCH_3)(S_2CN(CH_3)_2)]^+$;

m/e 131[$(S_2C_3CH_3HCH_3)]^+$

Elemental Analysis for $NiC_8H_{13}S_4N$:-

Calculated: %C=31.0, %N=4.5, %H=4.2

Observed: Not obtained

[(dithio-acetylacetonato)(N,N-diethyldithiocarbamato)nickel(II)]

[$Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)$] $NiC_{10}H_{17}S_4N$

The composite complex was prepared by a directly analogous experimental method to that discussed previously in the synthesis of [$Ni(S_2CN(CH_3)_2)(S_2C_3CH_3HCH_3)$]. [$Ni(S_2CN(C_2H_5)_2)_2$] (0.086g, 0.24mmole) and [$Ni(S_2C_3CH_3HCH_3)_2$] (0.078g, 0.24mmole) were heated in N_2 flushed toluene (50ml) at 110°C for a period of ten hours. Subsequent column chromatographic isolation of the hybrid product and recrystallisation from a mixture of dichloromethane: petroleum ether (60/80) in air yielded wine-coloured crystals of the desired [$Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)$] product.

Equilibrium yield=80%, Recrystallised yield=0.118g(70%)

Mass spectrum: m/e 337[$Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)$]

m/e 131[$(S_2C_3CH_3HCH_3)]^+$

Elemental Analysis for $NiC_{10}H_{17}S_4N$

Calculated: %C=35.5, %N=4.1, %H=5.1

Observed: %C=35.5, %N=4.2, %H=5.2

[(dithio-acetylacetonato)(N,N-di-isopropyldithiocarbamato)nickel(II)]

[Ni($S_2C_3CH_3HCH_3$)($S_2CN(i-C_3H_7)_2$)] $NiC_{12}H_{21}S_4N$

The hybrid complex was prepared in a manner analogous to that conducted in the synthesis of [Ni($S_2CN(CH_3)_2$)($S_2C_3CH_3HCH_3$)]. This involved the direct interaction of [Ni($S_2CN(i-C_3H_7)_2$)$_2$] (0.039g, 0.12mmole) and [Ni($S_2C_3CH_3HCH_3$)$_2$] (0.05g, 0.12mmole) in N_2 flushed toluene (45ml) at 110°C for a period of 13 hours. Following column chromatography and recrystallisation of the hybrid complex from a mixture of dichloromethane: petroleum ether (60/80) in air, wine-coloured crystals were obtained.

Equilibrium yield=75%, Recrystallised yield=0.054g(60%)

Mass spectrum: m/e 365[Ni($S_2C_3CH_3HCH_3$)($S_2CN(i-C_3H_7)_2$)]$^+$

m/e 131[($S_2C_3CH_3HCH_3$)]$^+$

Elemental Analysis for $NiC_{12}H_{21}S_4N$

Calculated: %C=39.4, %N=3.8, %H=5.8

Observed: %C=39.1, %N=4.1, %H=5.5

[(dithio-1-benzoylacetonato)(N,N-di-isopropyldithiocarbamato)nickel(II)]

[Ni($S_2C_3PhHCH_3$)($S_2CN(i-C_3H_7)_2$)] $NiC_{17}H_{23}S_4N$

The hybrid complex was synthesised by repetition of the basic experimental method employed in the preparation [Ni($S_2C_3CH_3HCH_3$)($S_2CN(i-C_3H_7)_2$)]. [Ni($S_2CN(i-C_3H_7)_2$)$_2$] (0.047g, 0.11mmole) and [Ni($S_2C_3PhHCH_3$)$_2$] (0.051g, 0.11mmole) were dissolved in oxygen-free toluene (50ml)

and heated for eleven hours at 110°C. Evaporation of the solvent produced a purple oil which yielded a solid when taken up in petroleum ether. No chromatographic treatment was required for the solid product as it consisted of only the desired [Ni(S$_2$C$_3$PhHCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)] composite complex. The solid was then recrystallised as before from a mixture of dichloromethane: petroleum ether (60/80) in air to yield a violet microcrystalline product.

Equilibrium yield=100%, Recrystallised yield=0.069g(70%)

Mass spectrum: m/e 427[Ni(S$_2$C$_3$PhHCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)]$^+$

m/e 193[Ni(S$_2$C$_3$PhHCH$_3$)]$^+$

Elemental Analysis for NiC$_{17}$H$_{23}$S$_4$N

Calculated: %C=47.7, %N=3.3, %H=5.4

Observed: %C=47.5, %N=3.2, %H=5.5

[(dithiobenzoylmethanato)(N,N-di-isopropyl dithiocarbamato)nickel(II)]

[Ni(S$_2$C$_3$PhHPh)(S$_2$CN(i-C$_3$H$_7$)$_2$)] NiC$_{22}$H$_{25}$S$_4$N

The above complex was synthesised by an analogous procedure to that used to obtain [Ni(S$_2$C$_3$PhHCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)]. [Ni(S$_2$CN(i-C$_3$H$_7$)$_2$)$_2$] (0.033g, 0.08mmole) and [Ni(S$_2$C$_3$PhHPh)$_2$] (0.045g, 0.08mmole) were dissolved in oxygen-free toluene (45ml) and heated for a period of 15 hours at 110°C. Removal of the solvent once again produced a purple oil, which was taken up in ether to produce a purple solid. This solid was recrystallised as previously reported for [Ni(S$_2$C$_3$PhHCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)].

Equilibrium yield=100%, Recrystallised yield=0.064g(80%)

Mass spectrum: m/e 489[$Ni(S_2C_3PhHPh)(S_2CN(i\text{-}C_3H_7)_2)$]$^+$

m/e 255[(S_2C_3PhHPh)]$^+$

Elemental Analysis for $NiC_{22}H_{25}S_4N$

Calculated: %C=53.9, %N=2.9, %H=5.1

Observed: %C=52.5, %N=2.8, %H=5.4

[(dithio-1,1,1-trifluoroacetylacetonato)(N,N-di-isopropyldithiocarbamato)nickel(II)]

[$Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)$] $NiC_{12}H_{18}S_4F_3N$

A method analogous to that employed in the synthesis of [$Ni(S_2C_3PhHPh)(S_2CN(i\text{-}C_3H_7)_2)$] was followed. [$Ni(S_2CN(i\text{-}C_3H_7)_2)_2$] (0.041g, 0.10mmole) and [$Ni(S_2C_3CF_3HCH_3)_2$] (0.043g, 0.10mmole) were reacted in boiling toluene (45ml, 110°C) for a period of ten hours under a nitrogen atmosphere. The hybrid complex was treated with ether in order to convert it from an oil to a solid purple product. The solid was then recrystallised from a dichloromethane: petroleum ether (60/80) mixture in air to obtain the hybrid complex as fine violet acicular crystals.

Equilibrium yield=100%, Recrystallised yield=0.056g(65%)

Mass spectrum: m/e 419[$Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)$]$^+$

m/e 185[$(S_2C_3CF_3HCH_3)$]$^+$

Elemental Analysis for $NiC_{12}H_{18}S_4F_3N$

Calculated: %C=34.3, %N=3.4, %H=4.3

Observed: %C=34.1, %N=3.1, %H=4.6

[(dithio-1,1,1-trifluorobenzoylacetonato)(N,N-di-isopropyldithiocarbamato)nickel(II)],

$[Ni(S_2C_3CF_3HPh)(S_2CN(i\text{-}C_3H_7)_2)]$ $NiC_{17}H_{20}S_4F_3N$

The hybrid complex was synthesised by the general experimental method employed above. This involved the interaction of $[Ni(S_2CN(i\text{-}C_3H_7)_2)]$ (0.032g, 0.08mmole) and $[Ni(S_2C_3CF_3HPh)_2]$ (0.04g, 0.08mmole) in toluene (40ml) at 110°C for a period of twenty hours. The hybrid product existed as a purple oil, but was apparently pure according to electrochemical and spectroscopic evidence.

Equilibrium yield=100% hybrid product

Mass spectrum: 482$[Ni(S_2CN(i\text{-}C_3H_7)_2)(S_2C_3CF_3HPh)]^+$

247$[(S_2C_3CF_3HPh)]^+$

[(dithio-acetylacetonato)(N,N-diethyldithiocarbamato)palladium(II)]

$[Pd(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ $PdC_{10}H_{17}S_4N$

This hybrid complex was prepared via the general experimental method employed in the synthesis of the corresponding $[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$.

$[Pd(S_2CN(C_2H_5)_2)_2]$ (0.055g, 0.137mmole) and $[[Pd(S_2C_3CH_3HCH_3)_2]$ (0.05g, 0.136mmole) were allowed to interact in toluene (50ml) at 110°C for a priod of 16 hours under a nitrogen atmosphere. On the removal of the solvent, the resulting solid was separated into its three constituents by column chromatography. The hybrid was

then recrystallised from a dichloromethane: petroleum ether mixture in air, yielding orange crystals.

Equilibrium yield=80%, Recrystallised yield=0.058g(55%)

Mass spectrum: m/e 385[$Pd(S_2CN(C_2H_5)_2)(S_2C_3CH_3HCH_3)$]$^+$

m/e 131[$(S_2C_3CH_3HCH_3)$]$^+$

Elemental Analysis for $PdC_{10}H_{17}S_4N$

Calculated: %C=31.1, %N=3.6, %H=4.4

Observed: %C=31.0, %N=3.7, %H=4.5

[(dithio-1,1,1-trifluoroacetylacetonato)(N,N-diethyldithiocarbamato)palladium(II)]

[$Pd(S_2C_3CF_3HCH_3)(S_2CN(C_2H_5)_2)$] $PdC_{10}H_{14}S_4F_3N$

The synthetic procedure was analogous to that carried out in the synthesis of [$Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)$]. [$Pd(S_2CN(C_2H_5)_2)$] (0.043g, 0.106mmole) and [$Pd(S_2C_3CF_3HCH_3)_2$] (0.051g, 0.106mmole) were dissolved in toluene (50ml) and reacted under a nitrogen atmosphere at 110°C for a period of twenty hours. Removal of the solvent once again produced an oil which was converted to a solid product via treatment with ether.

Recrystallisation from a mixture of dichloromethane: petroleum ether in air yielded scarlet rhombic crystals.

Equilibrium yield=100%, Recrystallised yield=0.048g(50%)

Mass spectrum: m/e 439[$Pd(S_2CN(C_2H_5)_2)(S_2C_3CF_3HCH_3)$]$^+$

m/e 185[$(S_2C_3CF_3HCH_3)$]$^+$

Elemental Analysis for $PdC_{10}H_{14}S_4F_3N$

Calculated: %C=27.3, %N=3.2, %H=3.2

Observed: %C=27.9, %N=3.2, %H=3.4

[(dithio-acetylacetonato)(N,N-diethyldithiocarbamato)platinum(II)]

[$Pt(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)$] $PtC_{10}H_{17}S_4N$

The platinum complex was prepared by an analogous procedure to that used in the synthesis of the corresponding [$Pd(S_2CN(C_2H_5)(S_2C_3CH_3HCH_3)$]. [$Pt(S_2C_3CH_3HCH_3)_2$] (0.069g, 0.15mmole) and [$Pt(S_2CN(C_2H_5)_2)_2$] (0.074g, 0.15mmole) were dissolved in toluene (55ml) and heated at 110°C for a period of 80 hours. The resulting solid was then separated into its three components by column chromatography. The hybrid product was isolated as a scarlet powder, but not recrystallised.

Equilibrium yield=65%, Mass obtained=0.022g(15%)

Mass spectrum: m/e 474[$Pt(S_2CN(C_2H_5)_2)(S_2C_3CH_3HCH_3)$]$^+$

m/e 131[$(S_2C_3CH_3HCH_3)$]$^+$

[(dithio-acetylacetonato)(N,N-dibutyldithiocarbamato)platinum(II)]

[$Pt(S_2C_3CH_3HCH_3)(S_2CN(C_4H_9)_2)$] $PtC_{14}H_{25}S_4N$

The synthetic path to this complex was similar to that employed in the preparation of [$Pt(S_2CN(C_2H_5)_2)(S_2C_3CH_3HCH_3)$]. [$Pt(S_2CN(C_4H_9)_2)_2$] (0.030g, 0.05mmole) and [$Pt(S_2C_3CH_3HCH_3)_2$] (0.023g; 0.05mmole) were mixed in toluene (35ml) at 110°C under a nitrogen atmosphere for a period of 72 hours. The resulting solid product was then separated into its relative components by column chromatography. The hybrid

complex was isolated as a scarlet powder but not recrystallised.

Equilibrium yield=60%, Mass obtained=0.012g(25%)

Mass spectrum: m/e 530[$Pt(S_2CN(C_4H_9)_2)(S_2C_3CH_3HCH_3)$]$^+$

m/e 131[$(S_2C_3CH_3HCH_3)$]$^+$

[(dithio-1,1,1-trifluoroacetylacetonato)(N,N-diethyldithiocarbamato)platinum(II)]

[$Pt(S_2C_3CF_3HCH_3)(S_2CN(C_2H_5)_2)$] $PtC_{10}H_{14}S_4F_3N$

The experimental procedure was parallel to that employed to obtain [$Pt(S_2CN(C_2H_5)_2)(S_2C_3CF_3HCH_3)$]. [$Pt(S_2C_3CF_3HCH_3)_2$] (0.031g, 0.055mmole) and [$Pt(S_2CN(C_2H_5)_2)_2$] (0.027g, 0.055mmole) were added to 40ml of toluene and heated at 110°C under a nitrogen atmosphere for 30 hours. On evaporating the toluene, the system became a red oil which was readily converted to the required solid hybrid product on the addition of ether. No chromatography was required.

Equilibrium yield=100%, Mass obtained=0.032g(55%)

Mass spectrum: m/e 528[$Pt(S_2CN(C_2H_5)_2)(S_2C_3CF_3HCH_3)$]$^+$

m/e 185[$(S_2C_3CF_3HCH_3)$]$^+$

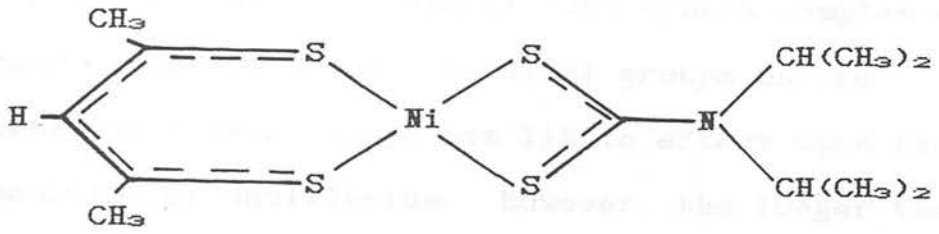
2.5 The Formation of [M($S_2CNR''_2$)(S_2C_3RHR')] Hybrid Complexes: The Position and Attainment of Scrambling Equilibria

As mentioned earlier, the rate at which the equilibrium distribution between reactants and hybrid product is achieved is dependent upon the reactant concentrations and the inductive effects of the alkyl substituents R and R' of the 1,3-dithio-β-diketonate ligand, but not significantly influenced by the choice of dialkyldithiocarbamate ligand. In the mixed complexes where R,R' = CH_3,CF_3; CH_3,Ph; Ph,Ph and Ph,CF_3, the hybrids were obtained more speedily than the analogous asymmetric complexes where R=R'=CH_3 and in qualitative yield.

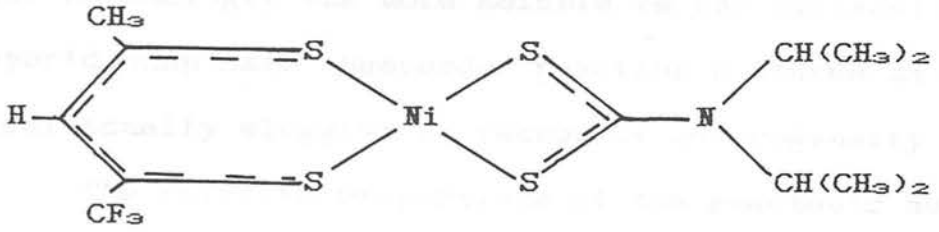
This is attributed to the additional stability gained from the reinforcement of mutually complementary π-acceptor (S_2C_3RHR') and π-donor ($S_2CNR''_2$) chelates. The larger Taft inductive parameters associated with CF_3 and Ph substituents, in comparison to that of CH_3 (see electrochemical discussion, Chapter 4), and thus, their greater electron-withdrawing ability, enable CF_3 or Ph substituted chelates to act as more efficient π-acceptors.

The relative influence on the equilibrium yield of the hybrid derived from the introduction of electron-withdrawing groups (CF_3 and/or Ph) to the 1,3-dithio-β-

diketonate ligand is clearly demonstrated in the examples shown below:-



[Ni($S_2C_3CH_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] = 75% Yield at Equilibrium (110°C)/13 hours



[Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] = 100% Yield at Equilibrium (110°C)/10 hours

Investigations into the effect on the rate of the scrambling process on replacing CH_3 substituents by CF_3 or Ph is most dramatically displayed by contrasting the two platinum-centred hybrids,

[Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_4H_9)_2$)] and

[Pt($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]. The production of these complexes involved similar reactant concentrations, 0.05mmole and 0.055mmole respectively but the rate of hybrid attainment was greatly enhanced when CF_3 replaced one CH_3 group on the 1,3-dithio-β-diketonate ligand. [Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_4H_9)_2$)] was obtained in a 60% equilibrium yield after reacting [Pt($S_2CN(C_4H_9)_2$)$_2$] and

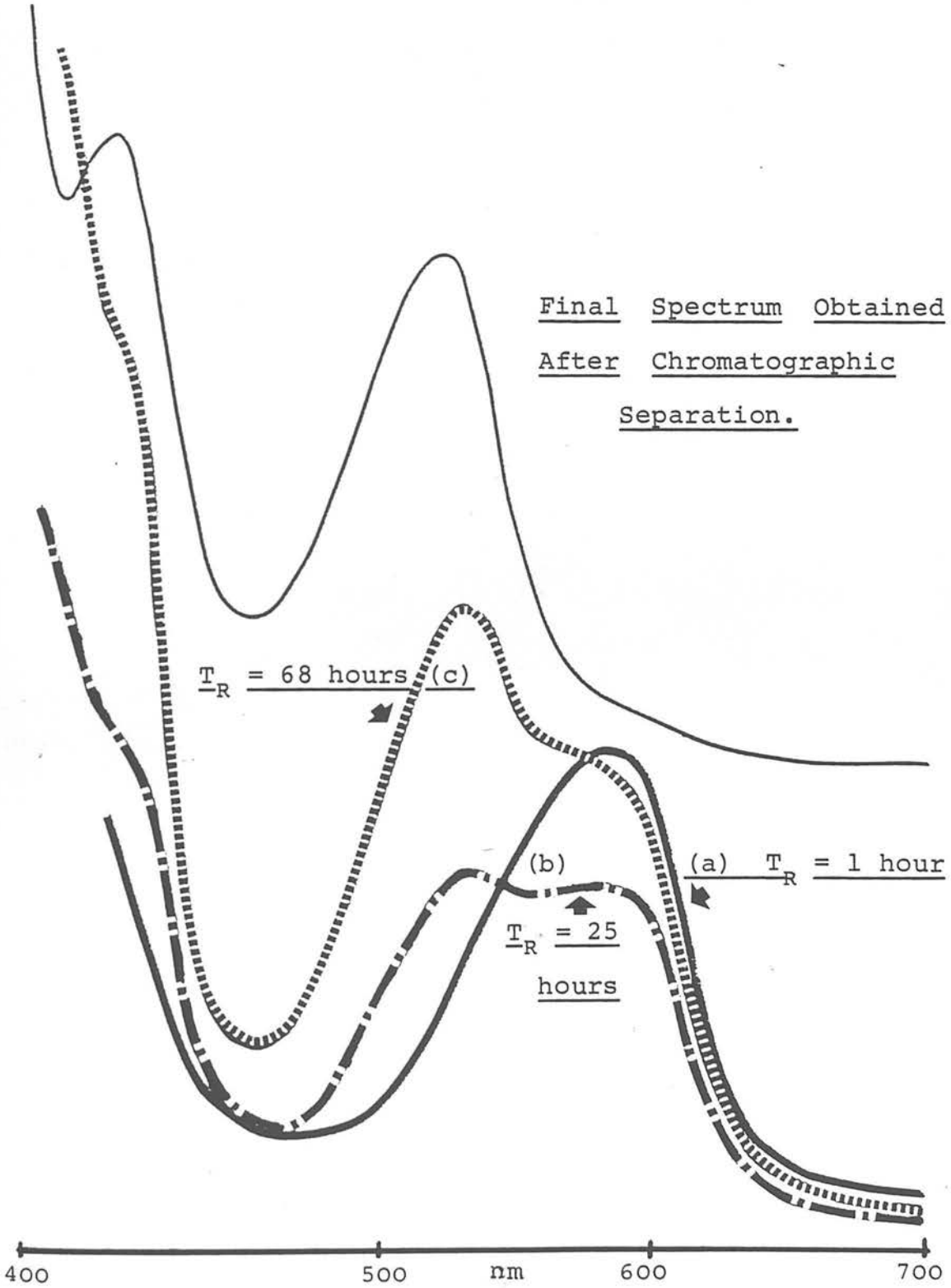
$[Pt(S_2C_3CH_3HCH_3)_2]$ in boiling toluene for 72 hours, much slower than $[Pt(S_2C_3CF_3HCH_3)(S_2CN(C_2H_5)_2)]$ which achieved its product distribution of 100% hybrid complex after 30 hours. Alteration of the alkyl groups on the dithiocarbamate ligand has little effect upon the position of equilibrium. However, the longer the alkyl chain, then the greater the solubility of the metal bis-N,N-dialkyldithiocarbamate starting material (and correspondingly the more soluble is the synthesised hybrid complex). Suspended reaction mixtures may be additionally sluggish by reason of heterogeneity.

The relative proportions of the reactants and hybrid complex present in the final solvent free reaction mixture, before chromatographic separation, were determined by ^1H nmr spectroscopy. In situ monitoring of the interacting system was also achieved by electronic spectroscopy. The progress of the synthesis to the hybrid product developed two new bands in the visible region which differed from those visible absorption bands of the two reactants, as exhibited by the reaction profile with time for the synthesis of $[Pt(S_2CN(C_4H_9)_2)(S_2C_3CH_3HCH_3)]$ (Figure 2.1).

A detailed account of the spectroscopic properties of the hybrid complexes, making direct comparisons with those features assigned to the parent complexes, $[M(S_2C_3RHR')_2]$ and $[M(S_2CNR''_2)_2]$, is presented in the following section. The X-ray structural parameters of

Figure 2.1 - Visible Spectra with Elapsed Reaction Time (T_R) for the Process :-

$[Pt(S_2C_3CH_3HCH_3)_2] + [Pt(S_2CN(C_4H_9)_2)_2] \rightleftharpoons 2\,[Pt(S_2C_3CH_3HCH_3)(S_2CN(C_4H_9)_2)]$



$[Ni(S_2C_3CF_3HCH_3)(S_2CN(C_2H_5)_2)]$ and $[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$ are contained in Chapter 3.

Electrochemical studies, in a dichloromethane medium, reveal a single one-electron reduction for all the hybrid complexes, situated at intermediate potentials relative to those observed for the first ligand-based reduction of the associated $[M(S_2C_3RHR')_2]$ complex and the more negative metal-based reduction of $[M(S_2CNR''_2)_2]$. Remarkably, voltammetry can often be a superior, sensitive and convenient test of the integrity of the product, or the composition of a mixture of these dithio-species. The implications of the electrochemical behaviour of the $[M(S_2CNR''_2)(S_2C_3RHR')]$ hybrid systems are discussed in Chapter 4.

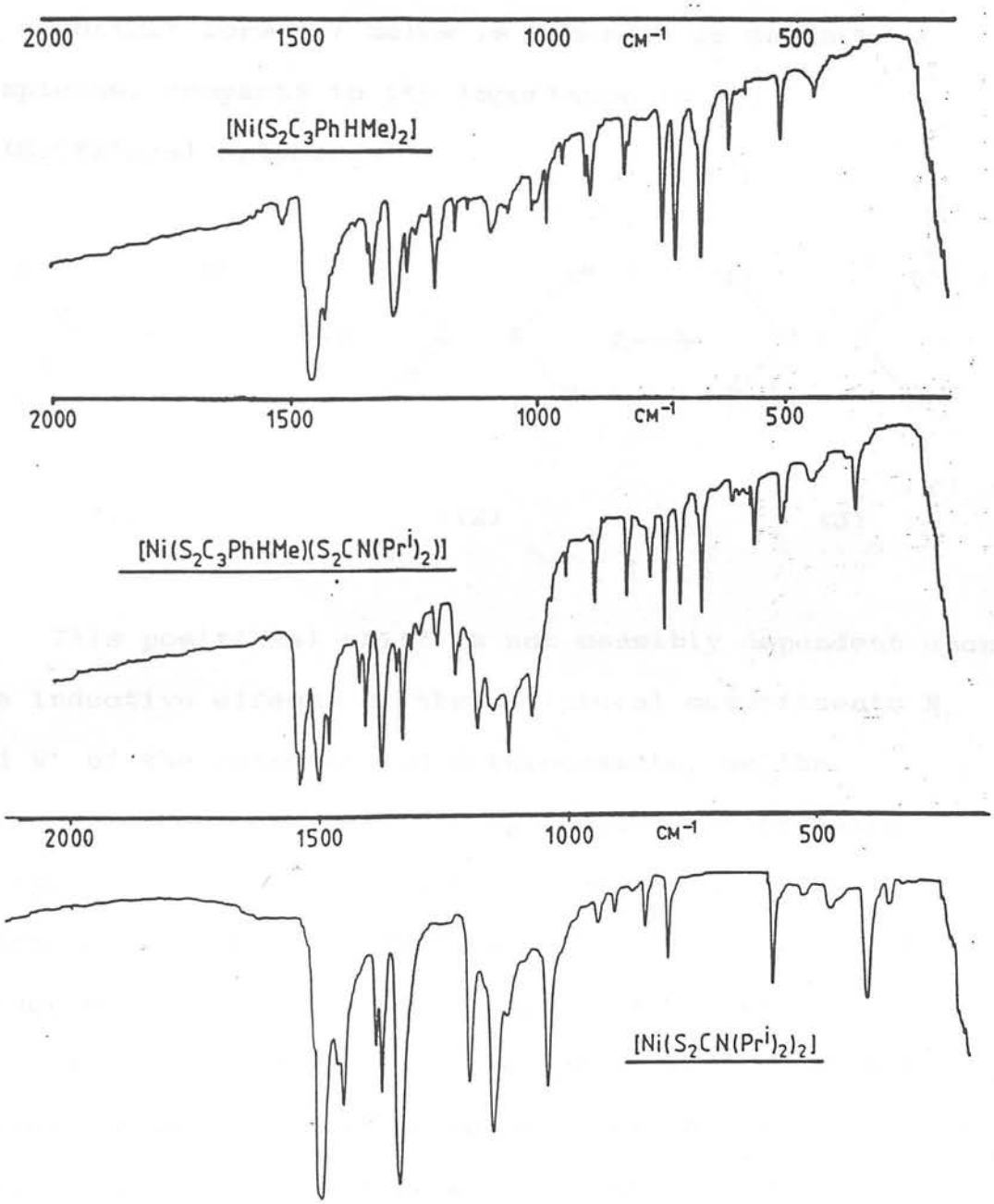
2.6 Spectroscopic Properties of $[M(S_2CNR''_2)(S_2C_3RHR')]$ Hybrids

(a) Infra-red Spectroscopy

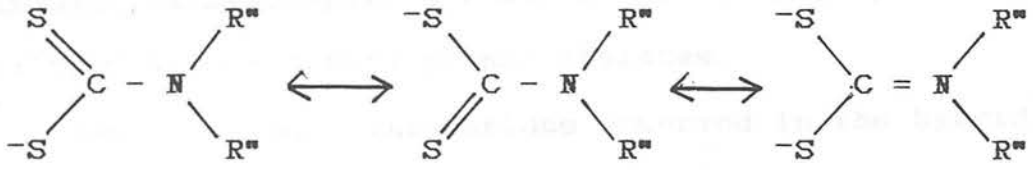
Infra-red spectroscopic examinations of the hybrid systems reveal spectra that consist of almost exact summations of the bands observed in the two parent compounds, $[M(S_2C_3RHR')_2]$ and $[M(S_2CNR''_2)_2]$. The three spectra in Figure 2.2 demonstrate this cumulative effect in the hybrid $[Ni(S_2C_3PhHCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$.

The complexity of the hybrid infra-red spectra limit our attention to six vibrational modes (Table 2.3), with

Figure 2.2 - Comparison of Parent and Hybrid Infra - red Spectra.



the analogous parent complex vibrational bands presented in parenthesis. For the newly discovered hybrid compounds, the most remarkable feature is the position of the ν(C==N) dithiocarbamate band which consistently shifts to higher energy, by approximately 15cm^{-1} in the Ni(II) complexes, compared to the parent bis-N,N-dialkyl-dithiocarbamates. This suggests that the participation of canonical form (3) below is enhanced in the hybrid complexes, compared to its importance in the [M(S_2CNR"$_2$)$_2$] compounds.



(1) (2) (3)

This positional shift is not sensibly dependent upon the inductive effects of the peripheral substituents R and R' of the adjacent 1,3-dithiochelate, as the introduction of two very strong electron-withdrawing groups to the (S_2C_3RHR') ligand does not progressively increase the hybrid ν(C==N) versus parent ν(C==N) shift to higher energy. (Compare compounds 3,4,5,6 in Table 2.3).

The close similarity of the other hybrid and parent system vibrational frequencies suggest that the electron density distributions within both hybrid 1,1-dithio- and 1,3-dithiochelate rings are relatively unchanged from the

parent compounds, showing that similar bond orders exist in both symmetric and mixed ring species. Although the positions of these vibrational bands in the hybrids generally mirror those found in the parent systems, many absorptions undergo vast intensity reductions in the hybrid, particularly those dithiocarbamate vibrational bands below 600cm^{-1} and to a lesser extent all bands below 900cm^{-1}. This observed decrease may be partly attributable simply to halving the density of dithiocarbamate groups, but more fundamentally we suspect to the larger dipole moment changes associated with asymmetrically coupled vibrations of the bis-N,N-dialkyldithiocarbamate planar chelates.

The very small alterations observed in the hybrid vibrational frequencies with respect to the parent absorptions are documented in Table 2.3 for some specific vibrations. These vibrational modes have largely been identified through the studies of Barraclough et al[42] and Siiman and Fresco[43], for metal bis-1,3-dithio-β-diketonates, and Chatt[41] and Ojima[44] for metal bis-N,N-dialkyldithiocarbamates.

Table 2.3 - Infra-Red Assignments of Vibrational Modes Observed in [[M($S_2CNR''_2$)(S_2C_3RHR')] Hybrid Complexess (KBr Disc, cm^{-1})

Hybrid Complex	1) ν(C=N)	2) ν(C=C) & ν(C—H)	3) ν(CSS) & ν(C=S)	4) π(C-H)	5) ν(C=S)	6) ν(M-S)
1) [Ni($S_2C_3CH_3HCH_3$)($S_2CN(CH_3)_2$)]	1542 (1534)	1478 (1483)	972 (967)	-	697 (697)	385 (384)
2) [Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)	1524 (1514)	1472 (1483)	992 (988) 908 (908)	820 (827)	703 (697)	389 (385)
3) [Ni($S_2C_3CH_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	1499 (1486)	1478 (1483)	1035 (1035) 943 (937) 905 (904)	838 (827)	706 (697)	392 (395)
4) [Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	1503 (1486)	1467 (1473)	1037 (1035) 937 (937) 910 (904)	845 (841)	683 (689)	384 (395)
4) [Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2$)]	1503 (1486)	1463 (1466)	1038 (1035) 929 (937) 908 (904)	836 (840)	691 (688)	378 (395)

Table 2.3 Continued/

Hybrid Complex	1) ν(C=N)	2) ν(C=C) & ν(C—H)	3) ν(CSS) & ν(C=S)	4) π(C-H)	5) ν(C=S)	6) ν(M-S)
6) [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	1502 (1486)	1492 (1489)	1037 (1035) 934 (937) 905 (904)	839 (847)	688 (693)	382 (395)
7) [Pd($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	1526 (1520)	1477 (1485)	990 (986) 908 (909)	820 (830)	704 (702)	359 (354)
8) [Pd($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]	1512 (1520)	1494 (1487)	991 (986) 912 (909)	850 (849)	698 (695)	363 (354)
9) [Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	1528 (1520)	– (1493)	990 (982) 908 (907)	821 (829)	707 (700)	362 (357)
10) [Pt($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]	1520 (1520)	1492 (1490)	993 (982) 912 (907)	851 (849)	699 (695)	362 (357)

Notes

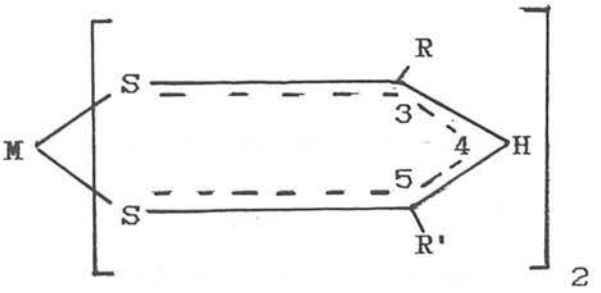
a) Vibrational frequencies 1), 3) and 6) are derived from the 1,1-dithiochelate, with 2), 4) and 5) contained in the 1,3-dithiochelate.

b) The spectra were obtained using a Perkin-Elmer 598 Infra-red Spectrometer.

(b) <u>^{1}H Nmr Spectroscopy</u>

Proton nmr spectroscopy proves to be a very useful technique by which the relative proportions of reactants and hybrid product can be readily identified, both during the reaction and in the final toluene-free reaction mixture. Moreover, interpretation of the hybrid resonances can be pursued, based on the small but systematic changes that occur relative to the chemical shifts of characteristic parent complex proton resonances.

Firstly, the parent metal bis-dithiocarbamate complexes exhibit alkyl resonances which are shifted to slightly higher frequency in comparison to those positions normally occupied by alkyl groups in saturated hydrocarbons, due to the influence of electronegative nitrogen. Equally, the parent metal bis-1,3-dithio-β-diketones show spectra that are consistent with the π-delocalised nature of the six-membered metallo-chelate ring. The introduction of stronger electron-withdrawing substituents, in place of CH_3, at positions 3 and 5 of the 1,3-dithio-ring results in further downfield shifts of the methine ring proton (attached to C-4 on the ring).



$[M(S_2C_3RHR')_2]$

The variation in chemical shift of the methine proton between the diamagnetic nickel, palladium and platinum 1,3-dithio complexes has been linked with presumed variations in the π-electron density of these delocalised ligands. In this respect, rather than invoking any special metal-chelate 'aromaticity', recognition must be given to the dominant deshielding effect of the sulphur atoms, in conjunction with the relative inductive effects of the substituents R and R'.

The relatively small effect of the complexing metal ion is clearly demonstrated by comparing the methine proton resonance for MS_2O_2 and MS_4 systems with the corresponding resonances for the free protonated ligands. Thus for $[Ni(SOC_3(OC_2H_5)HCH_3)_2]$ and $[M(S_2C_3(OC_2H_5)HCH_3)_2]$ complexes, where M = Ni, Pd, Pt, investigated by Hendrickson and Martin[29,45] in $CDCl_3$, one finds:-

i) $[Ni(SOC_3(OC_2H_5)\underline{H}CH_3)_2]$ = 5.76 ppm and free HSO ligand = 5.75 ppm.

ii) $[Ni(S_2C_3(OC_2H_5)\underline{H}CH_3)_2]$ = 6.59 ppm,
$[Pd(S_2C_3(OC_2H_5)\underline{H}CH_3)_2]$ = 6.59 ppm,
$[Pt(S_2C_3(OC_2H_5)\underline{H}CH_3)_2]$ = 6.58 ppm and free HS_2 ligand = 6.44 ppm.

The collection of comprehensive nmr data (particularly ^{13}C) for the metal bis-1,3-dithio-β-diketonates has proved challenging. Indeed, earlier workers were defeated by the relative insolubility of many of these complexes, even in

CD_2Cl_2, the most suitable solvent. By contrast, nmr studies of most metal bis-N,N-dialkyldithiocarbamates can be completed in a range of deuterated solvents. In the present study, the spectra of many parent 1,3-dithiochelates have largely been elucidated after helpful comparison with the spectra of the freely soluble hybrid complexes.

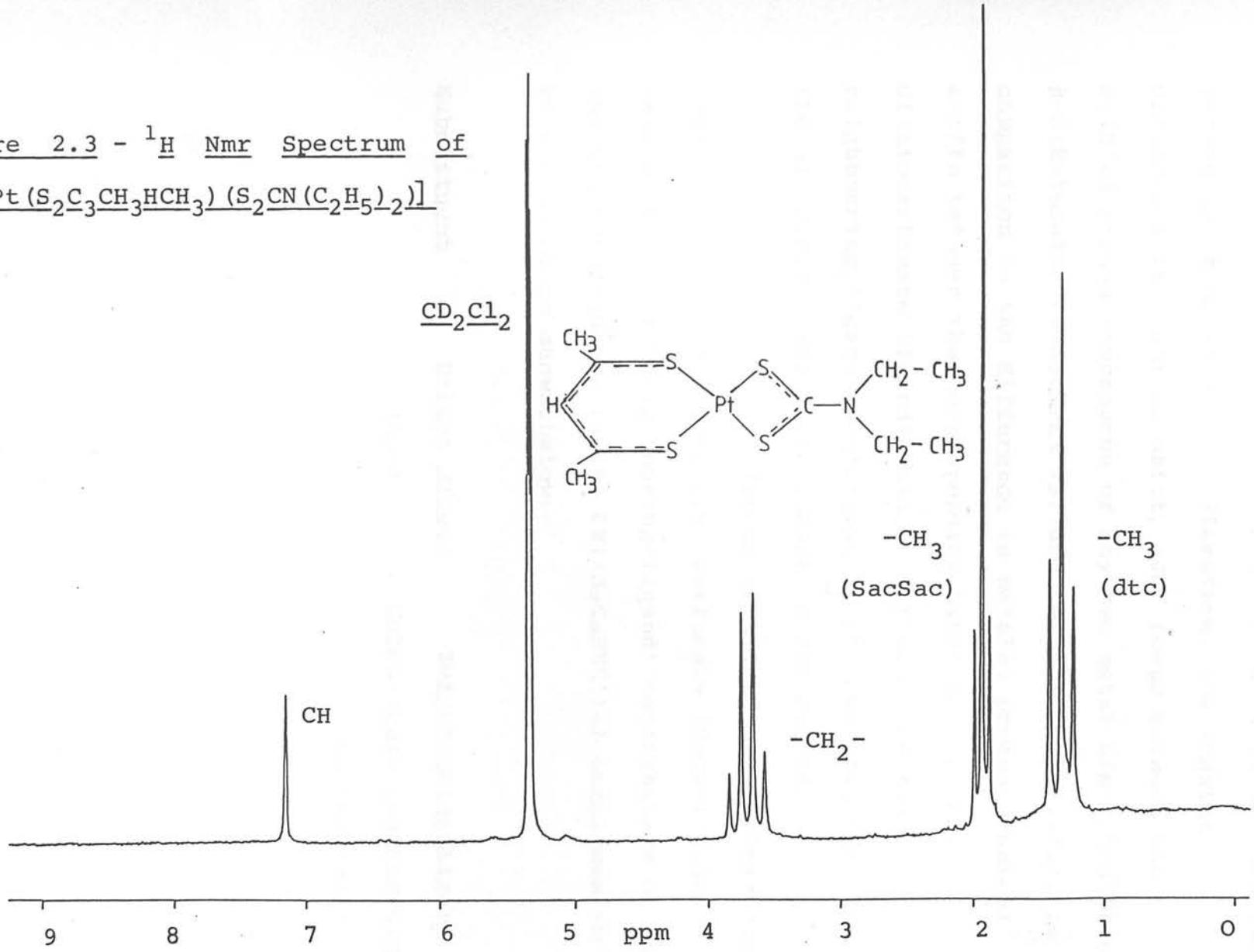
The ^1H nmr spectra of the hybrids exhibit signals readily related to those observed in the two parent complexes. Figure 2.3 shows the spectrum of $[Pt(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ a typical system.

Dithiocarbamate N-alkyl resonances are shifted to higher frequencies in the hybrids, $\Delta\delta$ (hybrid-parent) = +0.05 to +0.14 ppm, reinforcing our previous postulate of greater weight of the $^{2-}S_2C{=}\overset{+}{N}R''_2$ canonical form of the 1,1-dithio-ligand, in the hybrid. This enhancement arises from electron-donation from the dithiocarbamate ligand to the 1,3-dithiochelate ligand opposite, which in turn causes the methine proton to shift to higher frequency from its original position in $[M(S_2C_3RHR')_2]$.

In examining the hybrid ^1H nmr chemical shift data for the methine proton in the systems $[Ni(S_2C_3RHR')(S_2CN(i\text{-}C_3H_7)_2)]$ (from R,R' = CH_3,CH_3 to CF_3,Ph), we have discovered a previously unconsidered 'neighbouring-ligand' contribution to the observed chemical shift of the methine proton in the $[M(S_2C_3RHR')_2]$ systems. Thus, if we arbitrarily assign the methyl substituents as offering zero contributions, we find that the Ph and/or CF_3

Figure 2.3 - ^{1}H Nmr Spectrum of

$[Pt(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$



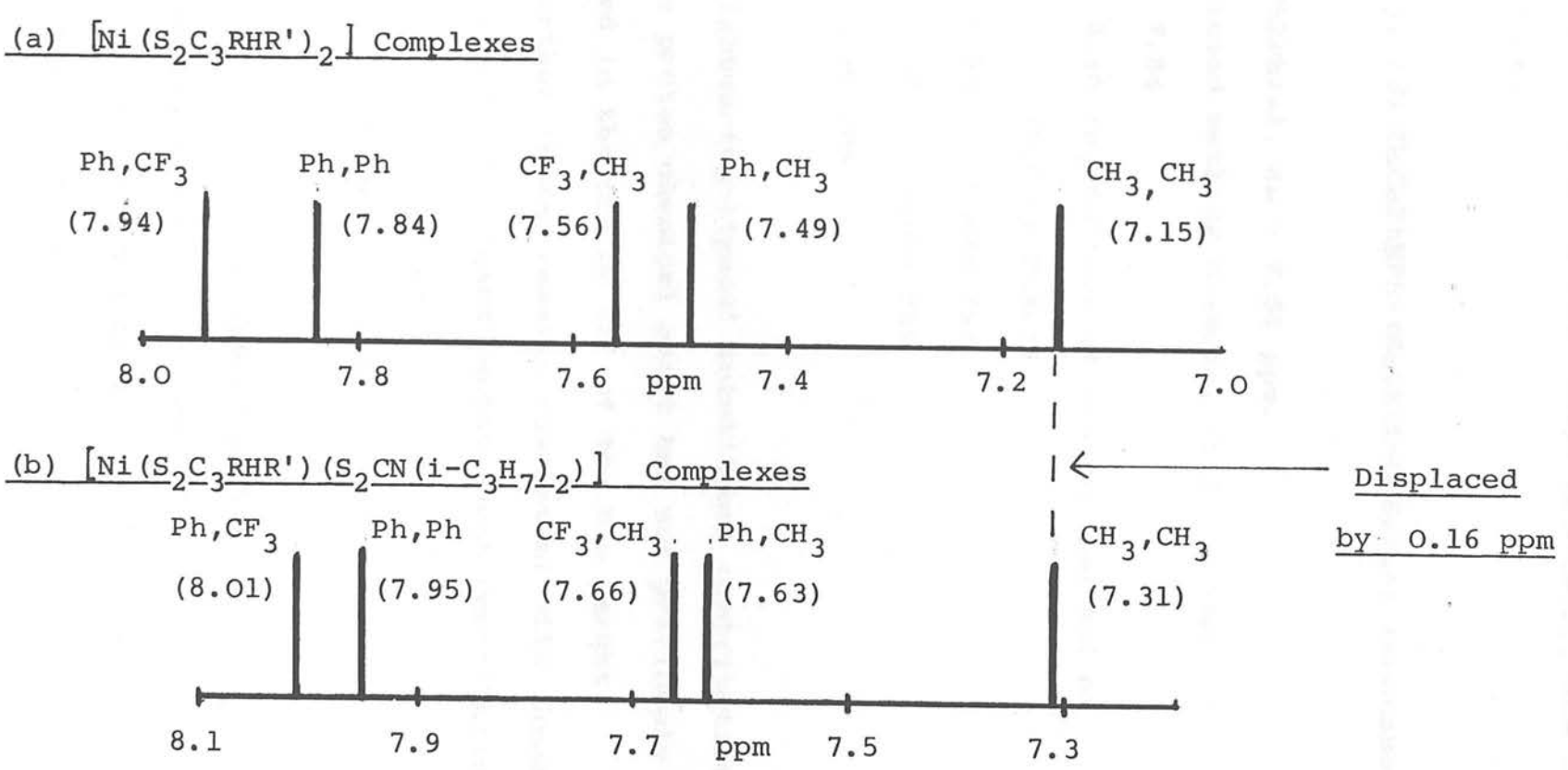
substituents on the ligand opposite make small but quantifiable 'neighbouring-ligand' contributions which help determine the observed chemical shift of the methine proton in $[M(S_2C_3RHR')_2]$. Therefore, the greater difference in chemical shift, $\Delta\delta_H$, found between the methine proton resonances of any two metal bis-1,3-dithio-β-diketonates $[M(S_2C_3RHR')_2]$ and $[M(S_2C_3R_{(a)}HR_{(b)})_2]$, in comparison to the difference in methine proton chemical shifts between the corresponding hybrids (constant dithiocarbamate ligand), can be explained by the neighbouring ligand substituent (R,R') contributions in the bis-parent, which are absent in the hybrid.

Our results for a series of nickel hybrids, where the ligand opposite is fixed, i.e. uniformly $(S_2CN(i\text{-}C_3H_7)_2)$, have enabled the 'neighbouring-ligand' contribution of Ph and CF_3 substituents in the $[Ni(S_2C_3RHR')_2]$ complexes to be evaluated as shown below:-

Substituent	Direct Effect (ppm)	Neighbouring-Ligand Substituent Contribution in Bis-Complexes (ppm)
CH_3	0	0
Ph	+0.32	+0.02
CF_3	+0.35	+0.06

The additive effect of these 'neighbouring substituent' parameters is displayed in Figure 2.4, by the

Figure 2.4 - Comparison of Methine Proton Chemical Shifts.



greater spread of bis-resonances. Predictions of methine resonances in new hybrids based on known [Ni(S_2C_3RHR')$_2$] chemical shifts can also be undertaken precisely, now that this is understood.

Experimentally, [Ni(S_2C_3PhHPh)(S_2CN(i-C_3H_7)$_2$)] resonance = 7.95 ppm.

For [Ni(S_2C_3PhHPh)$_2$], δ_H = 7.84 ppm.

Thus the predicted methine chemical shift in the hybrid ⇒ 7.84

+ 0.16 (aquisition of the dtc instead of ($S_2C_3CH_3HCH_3$))

- 0.02 (- remote Ph)

- 0.02 (- remote Ph)

7.96 ppm

These 'neighbouring-ligand' substituent contributions to the methine proton chemical shift had not previously been recognised in the proton nmr of the bis-parent complexes. Further 'H nmr results consistent with these quantified 'neighbouring-ligand' substituent contributions have also been observed in the [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)] complexes (M=Ni,Pd,Pt), examined in Chapter 5.

A notable aspect of these hybrid proton nmr studies concerns the persistent shifts to lower frequency of the methyl resonances of the 1,3-dithio-chelate, in moving from the bis-parent to the hybrid (lower frequency shifts

are not anticipated where π-electron density has increased). These shifts are rather puzzling, especially the relatively large displacements of the platinum-centred species [Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)] and [Pt($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)], which shift by 0.20 and 0.40 ppm from their respective bis-1,3-dithiochelates (see Figure 2.5).

Discontinuous methyl proton chemical shift behaviour of the 5d derivatives, compared to the 3d and 4d congeners, has also been encountered in the tris-complexes [M(SacSac)$_3$], M=Co, Rh, Ir [46]. Thus, while a "5d amplification factor" is familiar, this does not explain the unexpected contrast between the methyl chemical shift of [M($S_2C_3RHCH_3$)$_2$] and the corresponding hybrid complex for any one metal (Ni, Pd or Pt).

In Table 2.4, proton nmr data collected for the hybrid systems are compared with the corresponding resonances measured for the two parent complexes [M(S_2C_3RHR')$_2$] and [M($S_2CNR"_2$)$_2$].

Figure 2.5 - Comparison of Methyl Proton Chemical Shifts

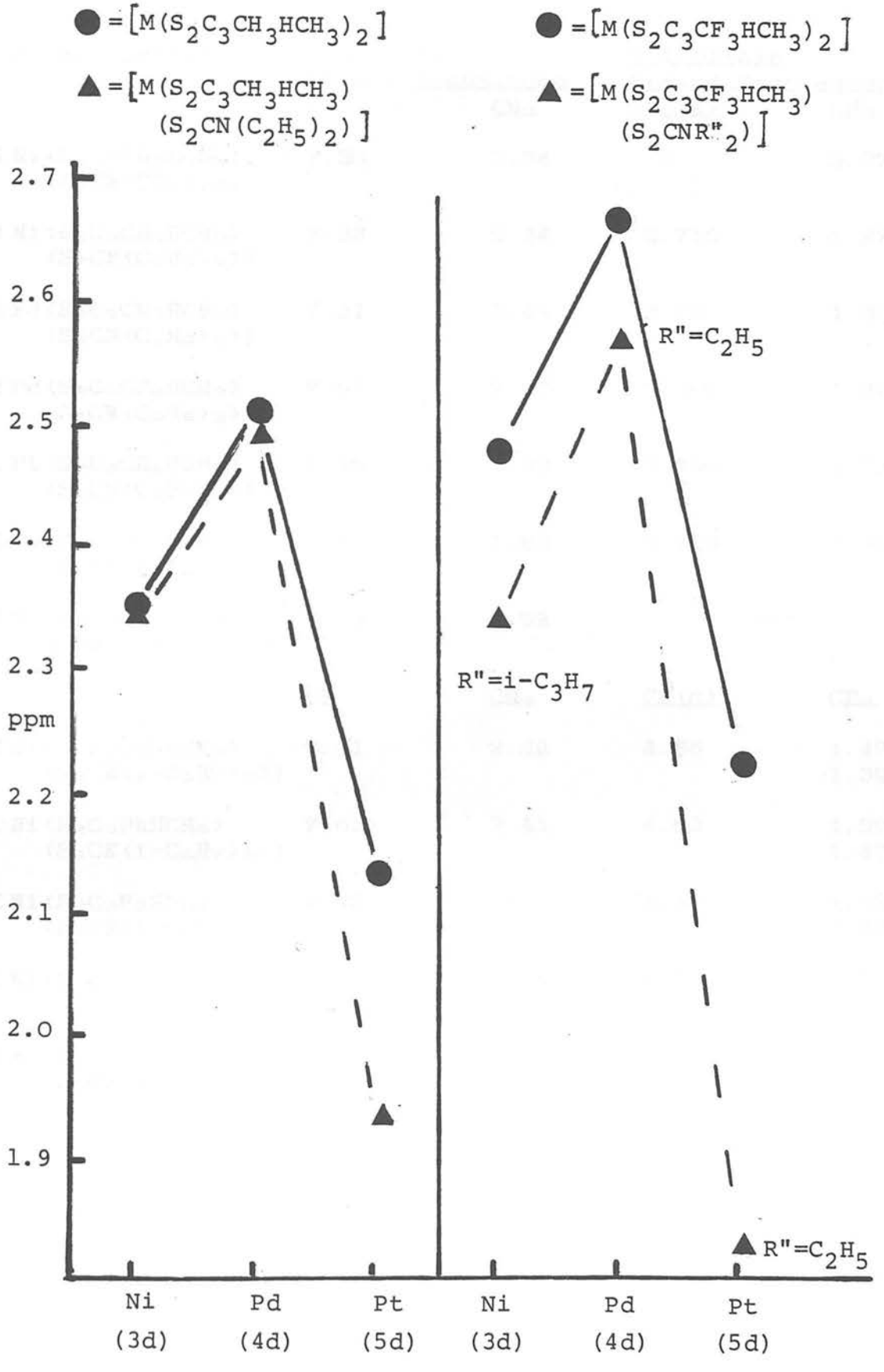


Table 2.4 - ^1H Nmr Resonances of Hybrid and Analogous Parent Complexes in CD_2Cl_2

Hybrid Complex	1,3-Dithio Ligand Resonances		1,1-Dithio Ligand Resonances	
	CH	CH_3	CH_2(a)	CH_3
[Ni($S_2C_3CH_3HCH_3$)($S_2CN(CH_3)_2$)]	7.33	2.34	-	3.27
[Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.33	2.34	3.715	1.27
[Pd($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.31	2.49	3.79	1.30
[Pd($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.68	2.57	3.805	1.32
[Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.15	1.93	3.705	1.33
[Pt($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.50	1.82	3.735	1.35
[Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_4H_9)_2$)] (b)	7.09	1.92	(c)	
	CH	CH_3	CH(d)	CH_3
[Ni($S_2C_3CH_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	7.31	2.32	4.56	1.47 1.39
[Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	7.63	2.41	4.58	1.50 1.42
[Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2$)]	7.95	-	~4.6	1.52 1.43
[Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	7.66	2.34	4.58	1.51 1.42
[Ni($S_2C_3PhHCF_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	8.01	-	~4.6	1.53 1.44

[M(S$_2$C$_3$RHR')$_2$] Complex	CH	CH$_3$
[Ni(S$_2$C$_3$CH$_3$HCH$_3$)$_2$]	7.15	2.35
[Ni(S$_2$C$_3$PhHCH$_3$)$_2$]	7.49	2.46
[Ni(S$_2$C$_3$PhHPh)$_2$]	7.84	-
[Ni(S$_2$C$_3$CF$_3$HCH$_3$)$_2$]	7.56	2.48
[Ni(S$_2$C$_3$PhHCF$_3$)$_2$]	7.94	-
[Pd(S$_2$C$_3$CH$_3$HCH$_3$)$_2$]	7.20	2.51
[Pd(S$_2$C$_3$CF$_3$HCH$_3$)$_2$]	7.60	2.67
[Pt(S$_2$C$_3$CH$_3$HCH$_3$)$_2$]	7.10	2.13
[Pt(S$_2$C$_3$CF$_3$HCH$_3$)$_2$]	7.50	2.22

[M(S$_2$CNR"$_2$)$_2$] Complexes	CH$_2$	CH$_3$
[Ni(S$_2$CN(CH$_3$)$_2$)$_2$]	-	3.17
[Ni(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]	3.595	1.22
[Pd(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]	3.715	1.27
[Pt(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]	3.595	1.29

	CH	CH$_3$
[Ni(S$_2$CN(i-C$_3$H$_7$)$_2$)$_2$]	4.47	1.43 1.35

Notes

The integral ratios of the respective proton resonances were found to be as expected in the hybrids and the parent complexes. The results in the above table were obtained on a Brücker WP80 spectrometer, operating at a

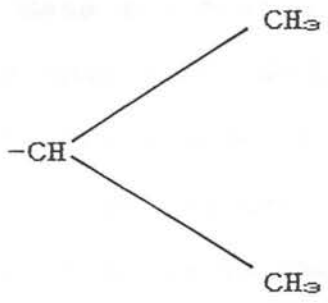
field strength of 80.13 MHz. CD_2Cl_2 solvent was used invariably and the operating temperature was 297K.

(a) The methylene and methyl resonances refer to the centres of the respective quartets and triplets.

(b) [Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_4H_9)_2$)] was dissolved in $CDCl_3$.

(c) The $-(CH_2)_3-CH_3$ system produces a complex pattern which is difficult to accurately interpret.

(d) The proton resonances noted at 4.47 to 4.6 ppm represent the centres of the septet obtained for the di-isopropyl group:-



^4J Pt-H Coupling Constants

The coupling constants for the interaction of the metal centre with the methyl protons of the 1,3-dithiochelate are almost identical (marginally increased) to those found in the parent complexes.

Complex	^{4} Pt-CH_3
[Pt($S_2C_3CH_3HCH_3$)$_2$]	8.4 Hz
[Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	8.9 Hz
[Pt($S_2C_3CH_3HCH_3$)($S_2CN(C_4H_9)_2$)]	8.9 Hz
[Pt($S_2C_3CF_3HCH_3$)$_2$]	7.7 Hz
[Pt($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)]	7.9 Hz

The platinum satellites associated with the methine ring proton are not observed as the signal strength is too weak.

(c) <u>^{13}C Nmr Data</u>

As previously mentioned, the solubility limitations of the parent $[M(S_2C_3RHR')_n]$ systems have seriously hindered the collection of their ^{13}C nmr data, with $[M(S_2C_3CH_3HCH_3)_2]$ (M=Ni, Pd, Pt)[47] and $[Rh(S_2C_3CH_3HCH_3)_3]$[48] the only systems for which partial data are available. Our synthesis of the more soluble hybrid complexes $[M(S_2C_3RHR')(S_2CNR''_2)]$ will enable us to study the dependence of ^{13}C chemical shifts on the congeneric 3d, 4d and 5d central ions and on perturbing substituents introduced to the periphery of the 1,3-dithiochelate ring. The effects of Ph and CF_3 substituents are demonstrated for the series of complexes $[Ni(S_2C_3RHR')(S_2CN(i\text{-}C_3H_7)_2)]$ (R/R' = CH_3/CH_3; CH_3/Ph; Ph/Ph; CF_3/CH_3) in Table 2.5 and Figures 2.8 and 2.9. ^{13}C chemical shift distinctions between the hybrids $[Ni(S_2C_3CH_3HCH_3)(S_2CNR''_2)]$ (R'' = C_2H_5, $i\text{-}C_3H_7$) and the relevant parent systems can also be readily evaluated from this table.

These proton decoupled spectra, were all obtained at 200 MHz, in CD_2Cl_2 at 303K. Figure 2.6 shows the ^{13}C spectrum of $[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ which displays features typical of the other hybrid systems.

Figure 2.6 - $^{13}C\ \{^{1}H\}$ Spectrum of

$[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$

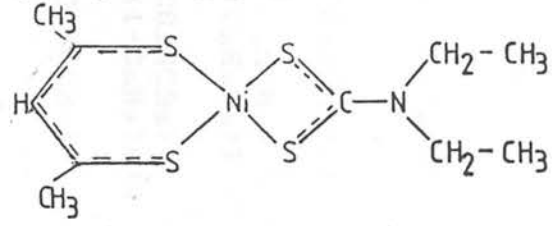
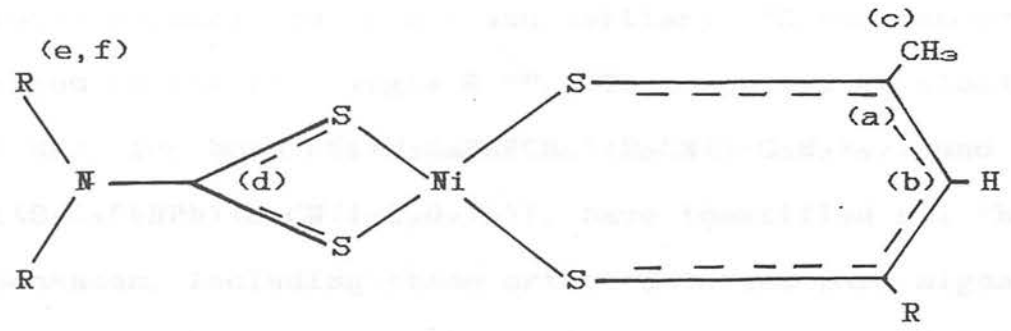


Table 2.5 $^{13}C\{^1H\}$ Nmr Data $[Ni(S_2C_3CH_3HR)(S_2CNR"_2)]$ Complexes (R = CH_3, CF_3)



Resonance(ppm) Complex	(a)	(b)	(c)	(d)	(e)	(f)
$[Ni(S_2CN(C_2H_5)_2)_2]$				206.2	44.15 (CH_2)	12.4 (CH_3)
$[Ni(S_2CN(C_3H_7)_2)_2]$				206.0	51.3 (CH)	19.8 (CH_3)
$[Ni(S_2C_3CH_3HCH_3)_2]$	184.4	131.8	32.7			
$[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$	180.8	132.7	33.2	203.8	44.5 (CH_2)	12.4 (CH_3)
$[Ni(S_2C_3CH_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$	180.85	132.7	33.35	202.9	51.6 (CH)	19.8 (CH_3)
$[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)$	185.8	130.1*	34.6	201.6	–	19.8 (CH_3)

* $^2J_{C-CF_3}$ (quartet observed) = 36.4 Hz

The ^{13}C signals were assigned by either retaining the proton coupling or by DEPT (Distortionless Enhancement by Polarization Transfer) experiments, which can distinguish between primary, secondary and tertiary ^{13}C resonances, via changes in the flip angle θ [49]. Thus spectra obtained at 360 MHz, for both [Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] and [Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2$)], have identified all the ^{13}C resonances, including those ortho, meta and para signals associated with the phenyl substituents. One-bond C-H coupling constants ($^1J_{CH}$) measured for these aromatic rings are in close agreement with the 158.5 Hz found by Maciel et. al.[50] for benzene. More importantly, the methine proton $^1J_{CH}$ coupling constants for [Ni($S_2C_3Ph\underline{H}CH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] (157.5 Hz) and [Ni($S_2C_3Ph\underline{H}Ph$)($S_2CN(i\text{-}C_3H_7)_2$)] (157.8 Hz) suggest that the extent of electron delocalisation within the [Ni(S_2C_3PhHR)] framework might be similar to that of benzene. This postulate is further strengthened by the ^{13}C chemical shift similarities of the tertiary carbons (bonded to methine proton) and benzene. The $^1J_{CH}$ couplings are listed below and shown in Figure 2.7 for [Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]. Further ^{13}C nmr studies are planned to determine the effect of the 4d and 5d ions (Pd, Pt) on the chemical shifts of the carbon resonances in the hybrid systems.

$^1J_{CH}$ Coupling Constants

1) [Ni($S_2C_3PhHCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]

CH (methine proton) = 157.5 Hz

pH (Ph substituent) = 161.9 Hz

oH (Ph substituent) = 161.3 Hz

mH (Ph substituent) = 160.7 Hz

2) [Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2$)]

CH (methine proton) = 157.8 Hz

pH (Ph substituent) = 161.8 Hz

oH (Ph substituent) = 161.4 Hz

mH (Ph substituent) = 160.7 Hz

Figure 2.7 - $^{1}J_{CH}$ Couplings Found in the Aromatic Region of $[Ni(S_2C_3PhHCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$

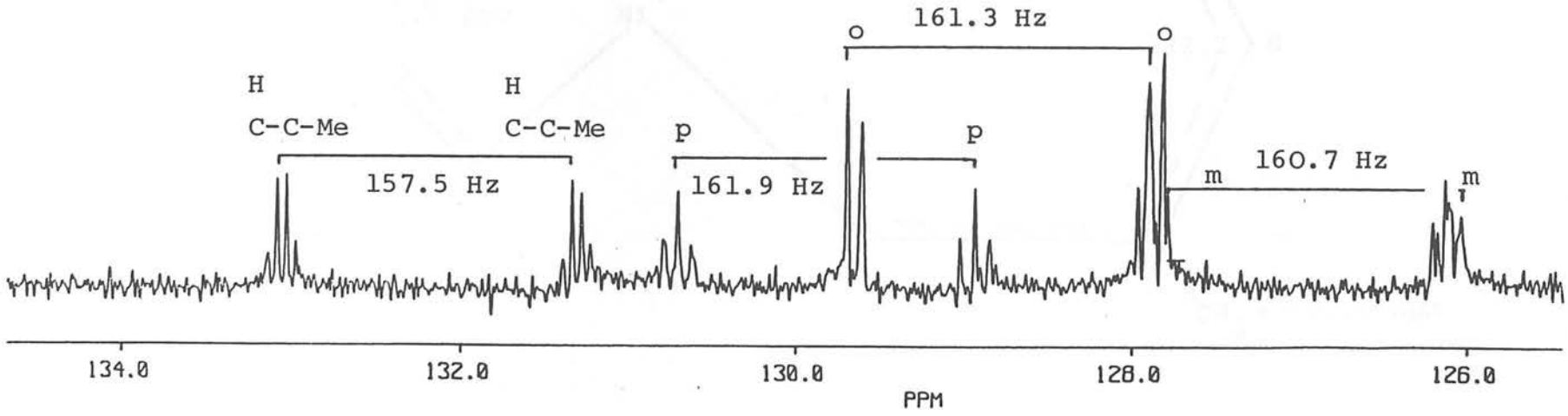


Figure 2.8 - $^{13}C\{^{1}H\}$ Nmr Data for $[Ni(S_2C_3PhHMe)(S_2CN(i\text{-}C_3H_7)_2)]$

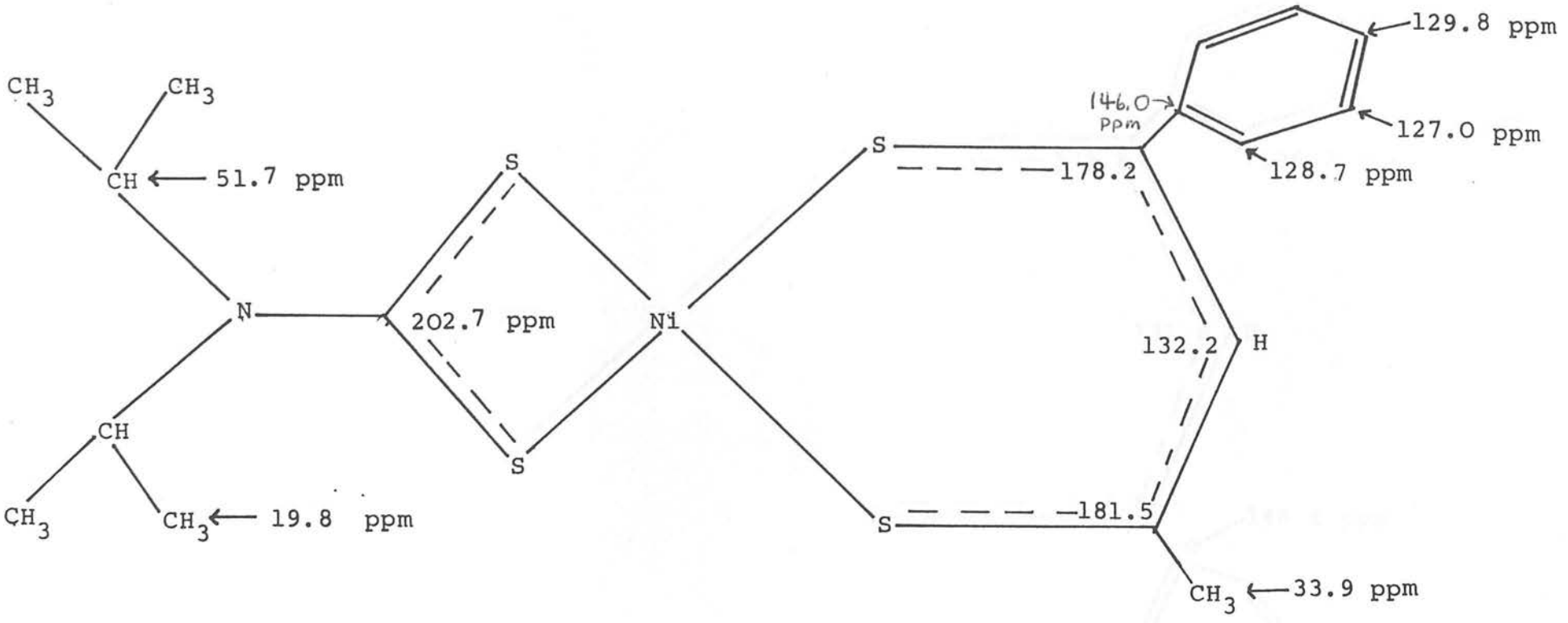
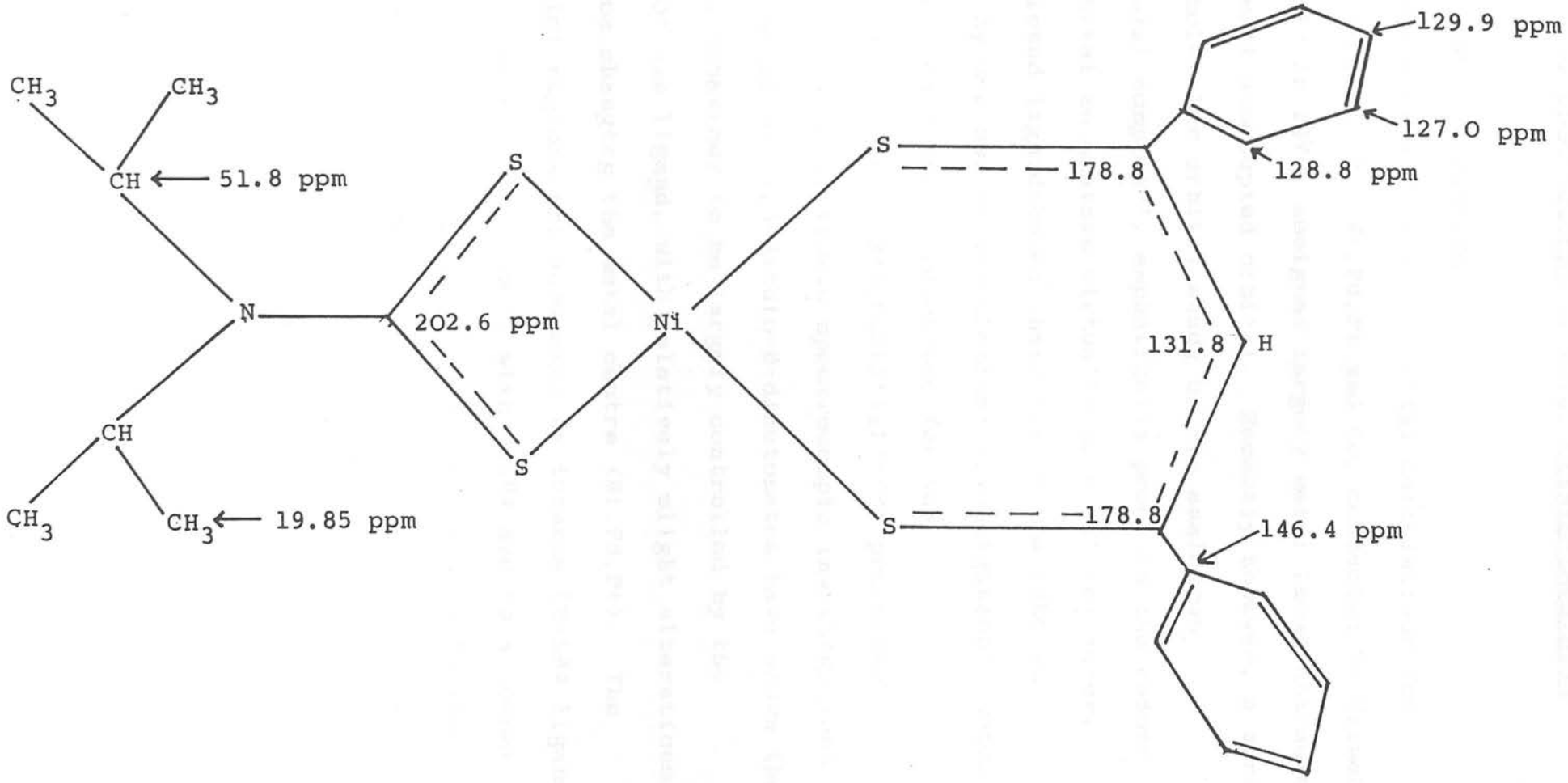


Figure 2.9 - $^{13}C\{^{1}H\}$ Nmr Data for $[Ni(S_2C_3PhHPh)(S_2CN(i\text{-}C_3H_7)_2)]$



(d) Electronic Spectroscopy of Metal Dithio-Complexes

(i) $[M(S_2C_3RHR')_2]$ Systems

Extended Hückel molecular orbital calculations for $[M(S_2C_3CH_3HCH_3)_2]$, M = Ni, Pd, Pt and Co, conducted by Siiman and Fresco[14] in 1970, assigned largely metal-based character to the lowest unoccupied orbital. Recently however, a more advanced molecular orbital study of the analogous $[Ni(S_2C_3H_3)_2]$ complex[5], emphatically predicts the redox-active orbital to contain virtually no metal character. This predicted ligand-based character of the LUMO is supported by our own electrochemical investigations, which reveal two ligand-based reductions for the $[M(S_2C_3RHR')_2]^{0/1-}$ and $[M(S_2C_3RHR')_2]^{1-/2-}$ processes.

Comprehensive electronic spectroscopic investigations for these metal bis-1,3-dithio-β-diketonates have shown the UV/visible behaviour to be largely controlled by the identity of the ligand, with relatively slight alterations observed on changing the metal centre (Ni, Pd, Pt). The ultra-violet regions are dominated by intense $L\pi \rightarrow L\pi^*$ ligand transitions above 31 000 cm^{-1}, with $M \rightarrow L\pi^*$ and to a lesser extent further intra-ligand transitions situated in the visible region of the spectrum. These charge transfer bands tend to obscure the weaker forbidden d-d transitions expected in the visible region.

(ii) [M(S$_2$CNR"$_2$)$_2$] Systems

Detailed assignments of the electronic spectra of metal bis-dialkyldithiocarbamates based on full M.O. calculations, have not been seriously attempted, due to difficulties caused by low energy charge-transfer bands which tend to obscure the expected weaker d-d transitions. Palladium and platinum bis-dialkyldithiocarbamates only show absorptions bands in the range between 22 200 - 45 400 cm^{-1}, with the corresponding nickel systems revealing additional extremely weak d-d transitions in the visible region with energies below 17 000 cm^{-1}. Alteration of the N-alkyl groups have little influence on the spectrum obtained for a constant metal centre.

The most intense high energy absorptions occurring at approximately 40 000 cm^{-1} in these complexes have been assigned to Lπ→Lπ* transitions[52] (as in [M(S$_2$C$_3$RHR')$_2$]), and relatively unaffected on changing the central metal ion. [M(S$_2$CNR"$_2$)$_2$] charge-transfer bands occur in the region of 28 500 - 32 300 cm^{-1} but their positive assignment as M→L or L→M transitions has not yet been completed.

iii) [M(S$_2$C$_3$RHR')(S$_2$CNR"$_2$)] Systems

The most striking feature of the hybrid spectra is the usual appearance of two absorption bands in the visible region, which generally do not coincide with the spectral bands of the starting compounds. Figures 2.10 - 2.12 show the spectra of the complexes [M(S$_2$C$_3$CH$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)]

(M = Ni,Pd,Pt) and the contrasting spectra of the parent bis-dithio complexes, at similar concentrations ($5x10^{-4}M$). The Ni and Pt systems clearly depict the two new bands but the second visible region absorption in the Pd hybrid is obscured by the strong absorption centred at 33 900 cm^{-1} and therefore only exists as a weak shoulder at 27 930 cm^{-1}. Reassuringly, the mixed system [Pd($S_2C_3CF_3HCH_3$)($S_2CN(C_2H_5)_2$)] clearly displays two visible bands at 18 790 and 24 040 cm^{-1}.

Overall, the hybrid spectra show a greater dependence upon the identity of the 1,3-dithio-β-diketonate ligand than the adjacent dialkyl-dithiocarbamate ligand, where alteration of the N-alkyl groups has virtually no effect on the observed hybrid spectrum. The hybrid bands in the visible region shift slightly but progressively to lower energy as the cumulative electron-withdrawing influence of R and R' increases, parallel to the behaviour previously encountered in the parent [M(S_2C_3RHR')$_2$] systems. This similarity is schematically depicted in Figure 2.13 for [Ni(S_2C_3RHR')($S_2CN(i-C_3H_7)_2$)] and [Ni(S_2C_3RHR')$_2$]. (The reader should concentrate on bands 1 and 2). These trends are also found in the palladium and platinum-centred hybrids (for our limited data).

Examination of the currently available hybrid spectra reveals an analogous band pattern in each case, regardless of M,R,R' or R". Corresponding bands have been identified, as far as possible, using the labels 1) to 5) in Table 2.6. No doubt these band envelopes conceal a great deal of

Figure 2.10 - Visible Spectra of Nickel Bis-Dithio-Ring Complexes. in Dichloromethane.

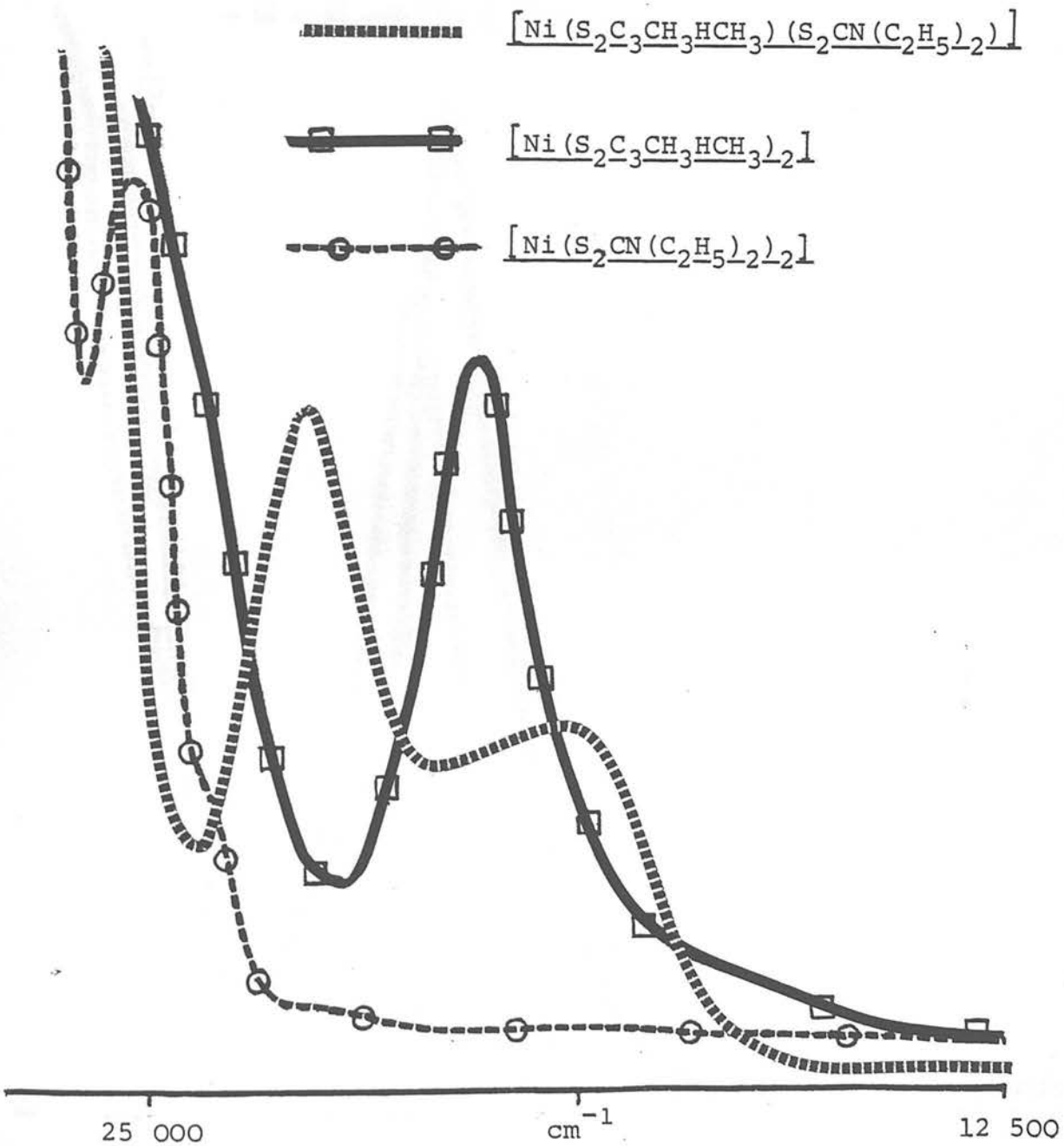


Figure 2.11 - Visible Spectra of Palladium Bis-Dithio-Ring Complexes in Dichloromethane.

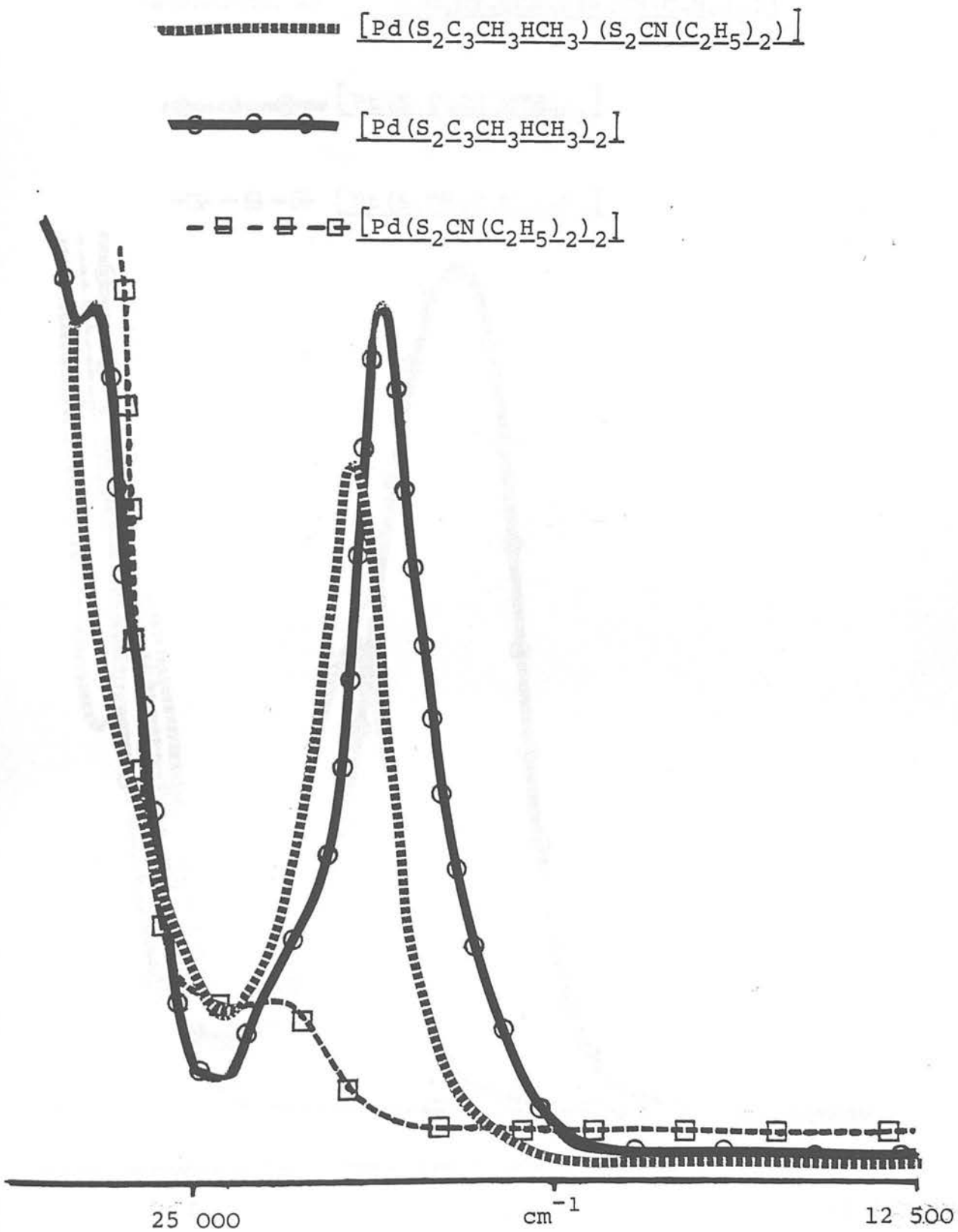
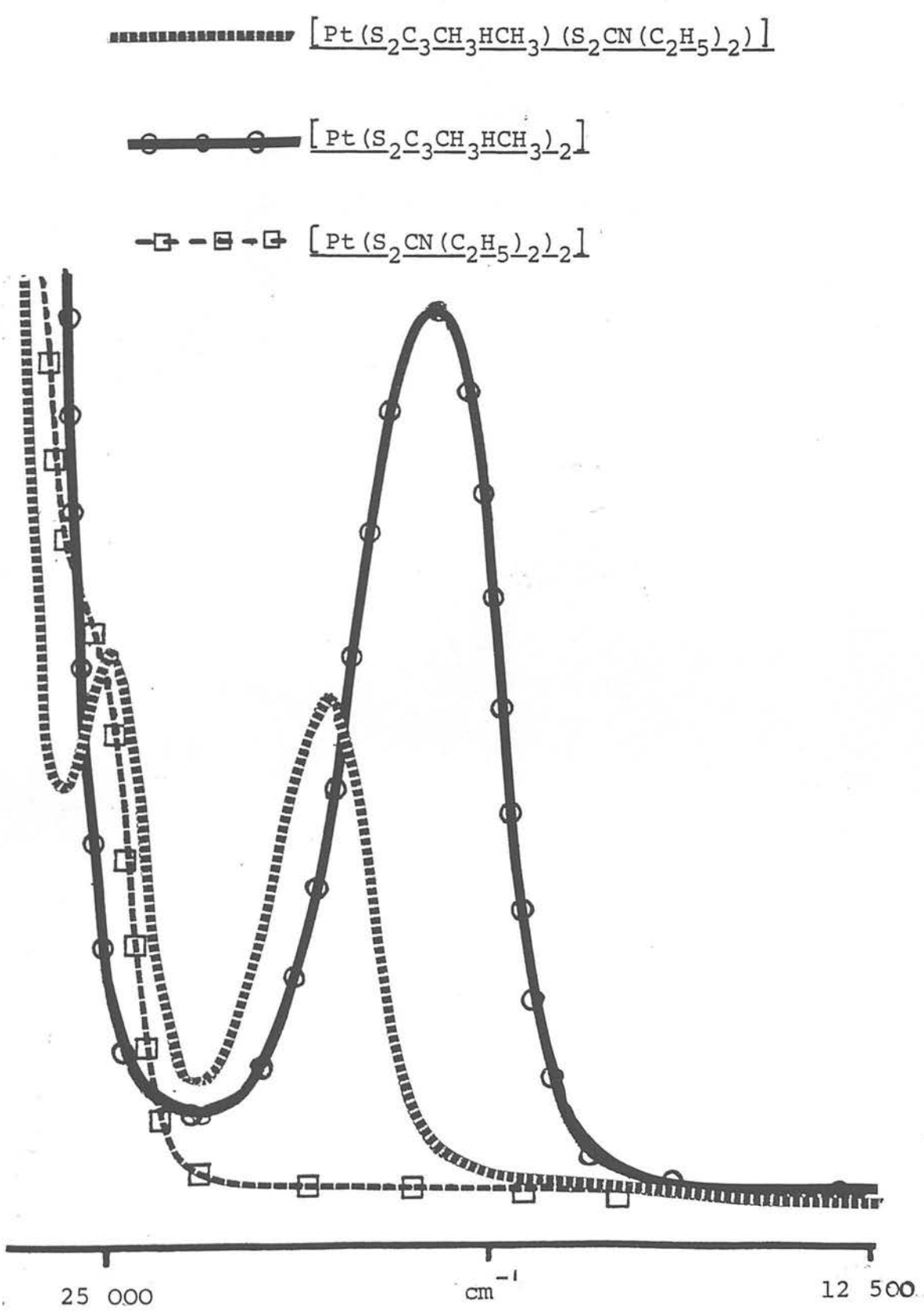


Figure 2.12 - Visible Spectra of Platinum Bis-Dithio-Ring Complexes in Dichloromethane.



complexity, but in the visible region at least (<25 000cm^{-1}) the hybrid spectra seem closely related to the parent 'SacSac' compounds (Figure 2.13).

Figure 2.13 - Schematic Summary of Electronic Spectroscopic Behaviour of $[Ni(S_2C_3RHR')(S_2CN(i\text{-}C_3H_7)_2)]$ and $[Ni(S_2C_3RHR')_2]$ in Dichloromethane. (——— Bands , — — — Shoulders)

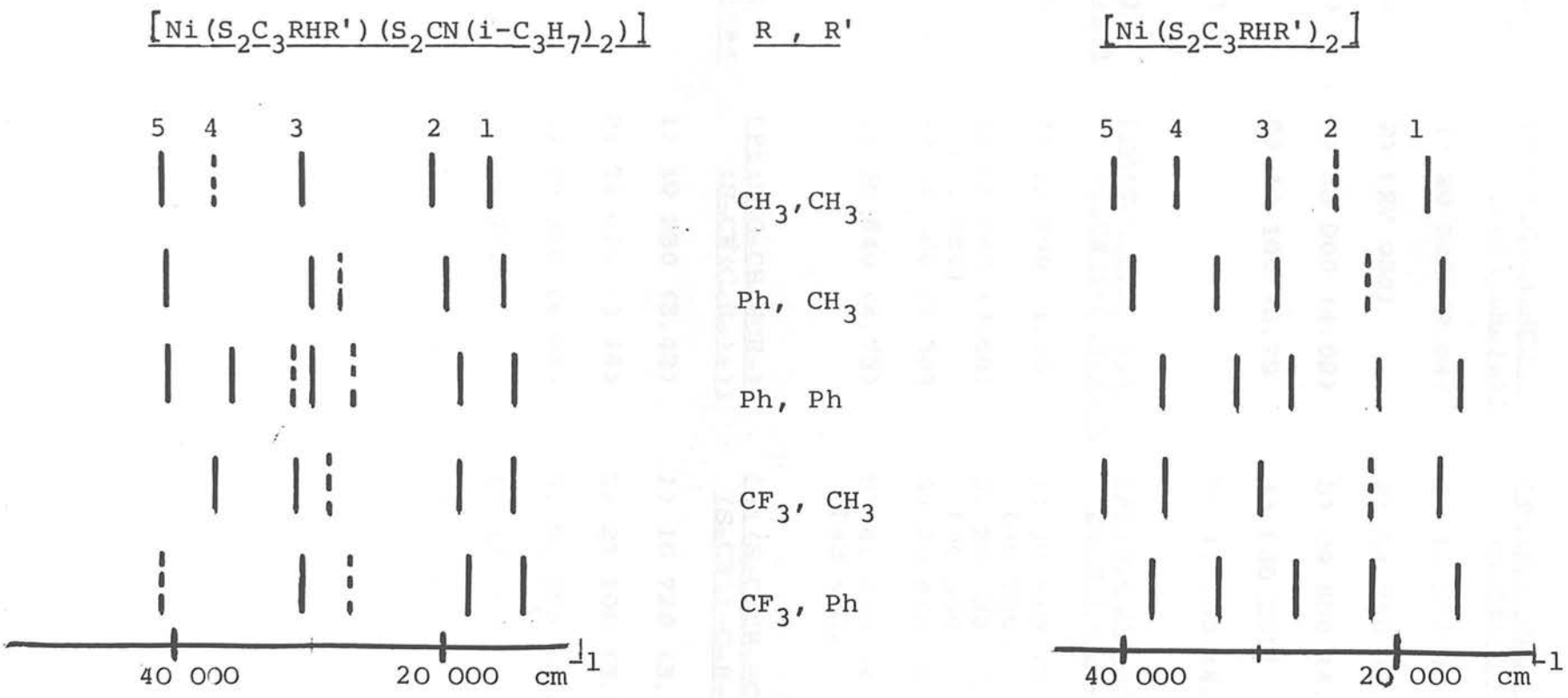


Table 2.6 Electronic Spectra of [M(S_2C_2RHR')($S_2CNR''_2$)] Complexes in CH_2Cl_2 (cm^{-1})

[Ni($S_2C_2CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	[Pd($S_2C_2CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]	[Pt($S_2C_2CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]
1) 16 860 (3.09)	1) 20 240 (2.94)	1) 19 270 (3.52)
2) 21 230 (3.38) [28 410]	2) [27 930]	2) 24 750 (3.55)
3) 30 770 (4.64)	4) 33 900 (4.02)	3) 29 850 (4.17)
4) [37 450]	5) 40 160 (3.79	4) [36 230]
5) 41 320 (4.57)		5) 41 150 (4.64)

[Ni($S_2C_2CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	[Pd($S_2C_2CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]	[Pt($S_2C_2CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]
1) 14 900 (3.30)	1) 18 790 (4.09)	1) 17 540 (3.51) [19 530]
2) 19 120 (3.05) [28 410]	2) 24 040 (3.68) [31 350]	2) 22 830 (3.62) [26 880]
3) 30 960 (4.72)	4) 34 360 (5.38)	3) 30 670 (4.39)
4) 37.170 (4.72)	5) 39 840 (4.73)	5) 41 320 (4.75) [43 480]

[Ni($S_2C_2CH_3HCH_3$)($S_2CN(CH_3)_2$)][a]	[Pt($S_2C_2CH_3HCH_3$)($S_2CN(C_4H_9)_2$)]	[Ni($S_2C_2CH_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]
1) 17 040	1) 19 230 (3.42)	1) 16 720 (3.11)
2) 21 320	2) 24 690 (3.44)	2) 21 100 (3.39)
3) 30 860	3) 29 760 (4.08)	3) 30 670 (4.68)
4)[37 310]	4)[35 970]	4)[37 040]
5) 41 490	5) 40 980 (4.55)	5) 41 150 (4.66)

[Ni(S$_2$C$_3$PhHCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)]	[Ni(S$_2$C$_3$PhHPh)(S$_2$CN(i-C$_3$H$_7$)$_2$)]	[Ni(S$_2$C$_3$PhHCF$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)][b]
1) 15 770 (3.14)	1) 14 990 (3.05)	1) 14 160
2) 20 080 (3.52)	2) 19 050 (3.50)	2) 18 250
[27 930]	[27 030]	[27 030]
3) 29 040 (4.71)	3) 29 850 (4.64)	3) 30 400
	[31 650]	
5) 40 820 (4.54)	4) 35 710 (4.01)	5)[40 980]
	5) 40 490 (4.31)	

Notes

i) The spectra were collected on a Pye-Unicam SP8-400 spectrometer, over a spectral range of 45 000 - 11 000 cm^{-1}.

iii) The absorptions presented in square brackets indicate shoulders.

iv) The parenthesised values refer to $\log_{10}e$, where e = extinction coefficient (mol^{-1} dm^3 cm^{-1}).

a) The complex [Ni(S$_2$C$_3$CH$_3$HCH$_3$)(S$_2$CN(CH$_3$)$_2$] was contaminated with a small amount of [Ni(S$_2$CN(CH$_3$)$_2$)$_2$].

b) [Ni(S$_2$C$_3$PhHCF$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)] exists as a purple oil and extinction coefficients have not been determined.

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CHAPTER 3

The Crystal and Molecular Structures of

[Ni(S$_2$C$_3$CH$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)] and

[Ni(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)]

3.1 Introduction

Crystallographic examinations of metal 1,3-dithio-β-diketonates have been almost exclusively conducted by Beckett and Hoskins. These studies involved the complexes $[M^{n}(S_2C_3CH_3HCH_3)_n]$, where M=Ni(II) [1], Co(II) [1], Fe(III) [2] and Rh(III) [3]. The familiar substituted metal 1,3-dithio-β-diketonates $[M^{n}(S_2C_3RHR')_n]$, where R,R'=Bu^t, Ph, CF_3, have been ignored with respect to crystallographic investigations, although the structures of the substituted systems $[Zn(S_2C_3(OC_2H_5)HCH_3)_2]$ and $[Ni(S_2C_3NH_2HNH_2)_2]$ have been determined[4,5].

The X-ray diffraction data collected from our nickel hybrids $[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ and $[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$ provide the first reported examples of crystallographically determined 1,3-dithio-1,1-dithio mixed-ligand complexes. These results allow the correlation of structual and geometric parameters discovered in the hybrid ligands, with those found in the parent complexes $[Ni(S_2C_3CH_3HCH_3)_2]$ and $[Ni(S_2CNR''_2)_2]$. Moreover the second example provides the first structural determination of the asymmetric $(S_2C_3CF_3HCH_3)$ ligand in any chemical context.

The crystallographic analysis of $[Ni(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]$ (I)[6] is readily interpreted, as full crystal structures are available for the parent compounds $[Ni(S_2CN(C_2H_5)_2)_2]$ (II) (Bonamico et

al.)[7] and [Ni(S$_2$C$_3$CH$_3$HCH$_3$)$_2$] (III) (Beckett and Hoskins)[1]. However, an analogous detailed analysis of [Ni(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)] (VI)[10] cannot be undertaken, as the X-ray structure of the parent bis-complex [Ni(S$_2$C$_3$CF$_3$HCH$_3$)$_2$] has not yet been reported, although a comprehensive crystallographic study of [Ni(S$_2$CN(i-C$_3$H$_7$)$_2$)$_2$] (VII) has been completed by Newman and White[11].

Structural and geometrical examinations of the second hybrid were attractive, with regard to establishing whether a stronger electron-withdrawing ligand would have a pronounced effect on the geometry of the neighbouring 1,1-dithiochelate, in comparison to (S$_2$C$_3$CH$_3$HCH$_3$) in [Ni(S$_2$C$_3$CH$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)]. Furthermore, the hybrid [Ni(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CN(i-C$_3$H$_7$)$_2$)] was useful in simultaneously determining the influence of the CF$_3$ substituent upon the geometry of the asymmetric six-membered metallo-chelate ring, contrasted with the symmetric SacSac ring reported in hybrid I, and the possibility of any structural trans- effects in the Ni-S bond lengths of the dithiocarbamate.

3.2 The Crystal and Molecular Structure of [(dithioacetylacetonato)(N,N-diethyldithiocarbamato) nickel(II)], [Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]

(a) Experimental

The hybrid complex [Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)] (I) was prepared as previously reported in Chapter 2. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation from a dichloromethane/60-80 petroleum ether mixture. A subsequent crystallographic examination (conducted by Dr. M.D. Walkinshaw) on one of these monoclinic plates of dimensions 0.35 x 0.25 x 0.15mm, showed the molecule to lie along a crystallographic two-fold axis.

Crystal Data - $C_{10}H_{17}NNiS_4$, M = 338.2, monoclinic, space group C2/c, a = 13.561(3), b = 12.700(2), c = 8.677(2) A°, β = 98.22(2)°, V = 1479 A°^{3}, Z = 4, Dc = 1.519 gcm^{-3}, MoKα radiation (λ = 0.71069 A°), μ = 18.4 cm^{-1}, T = 293K, R = 0.027.

The fractional co-ordinates for all atoms are given in Table 3.1. Bond lengths and angles are presented in Table 3.2 and a drawing of the asymmetric molecule is shown in Figure 3.1.

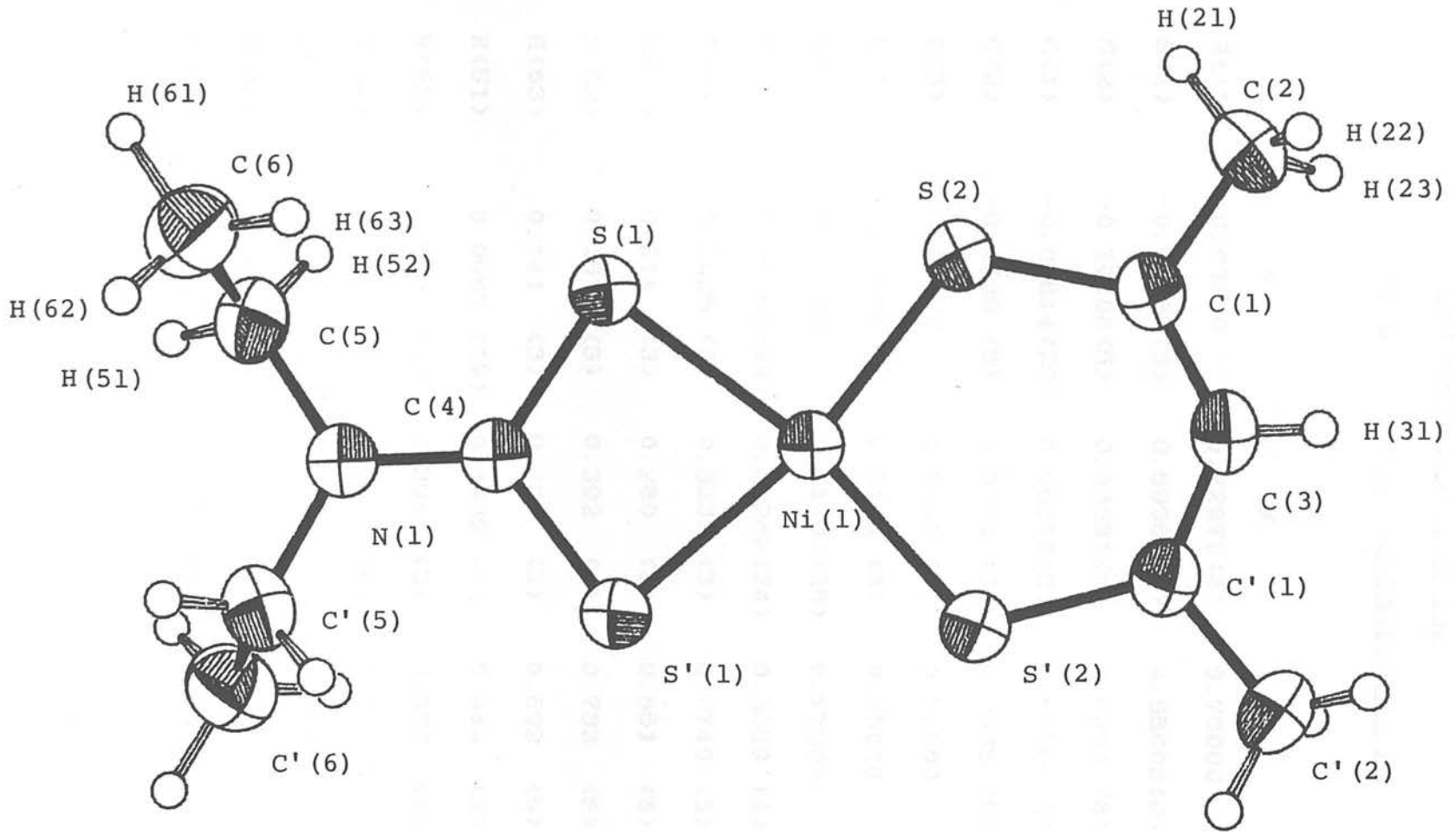


Figure 3.1 - [Ni($S_2CN(C_2H_5)_2$)($S_2C_3CH_3HCH_3$)]

Table 3.1 Fractional Coordinates of Atoms (with Standard Deviations for [Ni(S$_2$C$_3$CH$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)]

	x	y	z
Ni(1)	0.00000	0.72972(3)	0.75000
S(1)	−0.09086(5)	0.59369(6)	0.65008(9)
S(2)	−0.10108(5)	0.83581(5)	0.62382(8)
C(1)	−0.07814(20)	0.96512(21)	0.6536 (3)
C(2)	−0.1539 (3)	1.0364 (3)	0.5635 (5)
C(3)	0.00000	1.0106 (3)	0.75000
C(4)	0.00000	0.5159 (3)	0.75000
N(1)	0.00000	0.41205(25)	0.75000
C(5)	0.07663(24)	0.35282(24)	0.8539 (4)
C(6)	0.1625 (3)	0.3235 (3)	0.7740 (5)
H(61)	0.214 (3)	0.280 (3)	0.851 (6)
H(62)	0.181 (3)	0.392 (4)	0.733 (5)
H(63)	0.141 (3)	0.280 (3)	0.692 (5)
H(51)	0.0987 (19)	0.3939 (22)	0.949 (3)
H(52)	0.053 (3)	0.294 (3)	0.902 (4)
H(31)	0.00000	1.076 (4)	0.75000
H(21)	−0.197 (3)	0.996 (4)	0.477 (5)
H(22)	−0.124 (3)	1.093 (4)	0.513 (6)
H(23)	−0.184 (3)	1.067 (3)	0.635 (5)

Table 3.2 Bond Lengths(A°) and Bond Angles (°) in

[Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]

Ni(1)	- S(1)	2.2246(8)	C(3)	- H(31)	0.83(3)
Ni(1)	- S(2)	2.1128(7)	C(4)	- N(1)	1.318(3)
S(1)	- C(4)	1.7151(23)	N(1)	- C(5)	1.480(4)
S(2)	- C(1)	1.684 (3)	C(5)	- C(6)	1.486(5)
C(1)	- C(2)	1.502 (5)	C(5)	- H(51)	0.99 (3)
C(1)	- C(3)	1.380 (4)	C(5)	- H(52)	0.94 (4)
C(2)	- H(21)	1.02 (5)	C(6)	- H(61)	1.05 (5)
C(2)	- H(22)	0.961 (5)	C(6)	- H(62)	0.98 (5)
C(2)	- H(23	0.89 (4)	C(6)	- H(63)	0.92 (4)

S(1)	- Ni(1)	- S(1)	78.10(3)		
S(2)	- Ni(1)	- S(2)	100.76(3)		
S(1)	- Ni(1)	- S(2)	90.64(3)		
Ni(1)	- S(1)	- C(4)	86.15(8)		
Ni(1)	- S(2)	- C(1)	116.77(10)		
S(2)	- C(1)	- C(2)	114.20(22)		
S(2)	- C(1)	- C(3)	127.61(21)		
C(2)	- C(1)	- C(3)	118.2 (3)		
C(1)	- C(2)	- H(21)	110.9 (26)		
C(1)	- C(2)	- H(22)	112.6 (29)		
C(1)	- C(2)	- H(23)	104.7 (28)		
H(21)	- C(2)	- H(22)	106.0 (39)		
H(21)	- C(2)	- H(23)	117.5 (38)		
H(22)	- C(2)	- H(23)	105.1 (40)		
C(1)	- C(3)	- H(31)	114.8 (22)		
C(1)	- C(3)	- C(1)	130.5 (3)		

S(1) - C(4) - N(1)	125.20	(17)
S(1) - C(4) - S(1)	109.61	(8)
C(4) - N(1) - C(5)	120.55	(20)
N(1) - C(5) - C(6)	111.9	(3)
N(1) - C(5) - H(51)	110.1	(16)
N(1) - C(5) - H(52)	114.8	(22)
C(6) - C(5) - H(51)	111.1	(16)
C(6) - C(5) - H(52)	110.3	(22)
H(51)- C(5) - H(52)	97.9	(27)
C(5) - C(6) - H(61)	109.6	(25)
C(5) - C(6) - H(62)	102.1	(28)
C(5) - C(6) - H(63)	108.9	(27)
H(61)- C(6) - H(62)	120.7	(37)
H(61)- C(6) - H(63)	106.2	(37)
H(62)- C(6) - H(63)	108.9	(38)
H(62)- C(6) - H(63)	108.9	(38)

(b) Results and Discussion

The crystal is composed of discrete neutral molecules of complex I, with the anticipated essentially planar but strongly asymmetric NiS_4 co-ordination. A two-fold crystallographic rotation axis passes through N(1), C(4), Ni, C(3) and H(31) and the measured inclination of the two ligand planes, defined by Ni, S(1), C(4), S'(1) and Ni, S(2), C(1), C(3), C'(1), S'(2), C'(1), S'(2), is 3.9°.

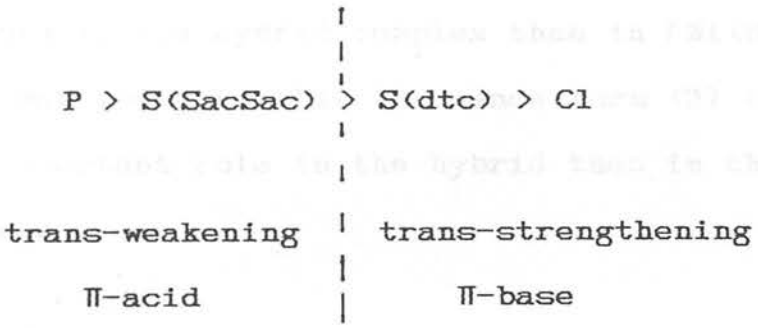
(i) The Nickel Co-ordination Geometry:

In this mixed-ligand system, the dtc (dithiocarbamate) S-Ni-S angle is only 78.1° and the corresponding SacSac angle is 100.8°, thus amplifying the difference in bite angles observed for the parent $[Ni(S_2CN(C_2H_5)_2)_2]$ and $[Ni(S_2C_3CH_3HCH_3)_2]$ (II and III). The effect of having dtc trans to SacSac is to further strengthen (shorten) the Ni-S (1,3-dithio) bond (ca. 2.156A° in the bis-parent) to 2.1128A° and weaken (lengthen) the Ni-S (1,1-dithio) bond (ca. 2.20A° in the bis-parent) to 2.2246A°.

Helpfully, the individual dtc and SacSac ligands may also be rigourously compared bound to identical moities in $Ni(S_2CN(C_2H_5)_2)(P(C_2H_5)_3)Cl$ (IV) (Chan et al., 1982)[8] and $Ni(S_2C_3CH_3HCH_3)(P(C_2H_5)_3)Cl$ (V) (Fackler and Masters, 1980)[9]. The intrinsic difference in dtc and SacSac Ni-S bond lengths is then seen to be about 0.08A° (i.e. 0.076

trans to Cl and 0.086 trans to $P(C_2H_5)_3$), but the observed difference is increased to 0.112A° in the present hybrid (and diminished to 0.044A° for the parent complexes) through the mutual trans influences of the two dithio ligands. We note for example that the SacSac Ni-S bond length in I (trans to dtc) resembles that trans to Cl in V, whereas the SacSac Ni-S bond in III (trans to another SacSac) resembles that trans to phosphine in V (cf. Table 3.4)

In summary, a consistent picture emerges for I to V allowing us to assign N,N-diethyldithiocarbamate a trans influence similar to Cl, and to assign SacSac a trans influence similar to $P(C_2H_5)_3$. These results fit with a structural 'trans effect' series such that:-



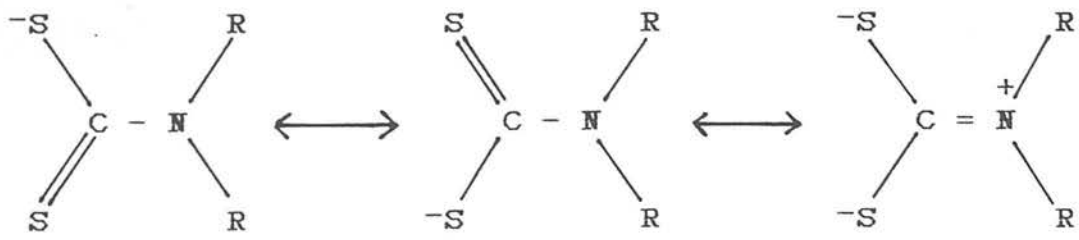
The intraligand S---S distances are 3.26A° (1,3-dithio) and 2.80A° (1,1-dithio), and the interligand S(1)---S(2) distance is 3.09A°. All these distances are less than the sum of the sulphur van der Waals radii of 3.48A° (Bondi, 1964)[12] and allow the possibility of direct S---S electronic interaction.

The shortest non-bonded intermolecular contact involving nickel is to the methylene groups (C5) which lie

approximately in the remaining two octahedral sites, with Ni---(C5) = 3.78A°, Ni---H(51) = 3.47A° and Ni---H(52) = 3.22A°. A very similar arrangement is found in the crystal packing of $[Ni(S_2CN(C_2H_5)_2)_2]$ (II), with a Ni---C (methylene) distance of 3.54A°. No electronic influence on the Ni^{2+} ion is ascribed to this packing arrangement in either case.

(ii) Ligand Geometry (1,1-dithio-chelate):

In the hybrid complex(I), the dithiocarbamate NCS_2Ni moiety is strictly planar (C_2 axis), and there is only slight rotation of the trigonal $N(C_2H_5)_2$ group from this plane. Marginally longer S-C bonds and a slightly shorter C-N bond in the hybrid complex than in $[Ni(S_2CN(C_2H_5)_2)_2]$ (II), may indicate that resonance form (3) below plays a more important role in the hybrid than in the symmetrical complexes.



(1) (2) (3)

An overall comparison of the structural data for the 1,1-dithio-ligand in complexes I and II reveals that there are very few structural and geometric differences.

Relevant bond lengths and angles for I, II and IV are compared in Table 3.3.

(iii) Ligand Geometry (1,3-dithio-chelate)

Relevant data for I, III and V are compared in Table 3.4. In the hybrid, the S-C and C-C bond lengths are identical to those found in $[Ni(S_2C_3CH_3HCH_3)_2]$ itself, suggesting that the ligand geometry is rather insensitive to the anticipated variation in charge distribution. The close planarity of the NiS_2C_3 chelate ring in the hybrid is notable since it is not crystallographically imposed, and significant folding across S_2---S_2' has been observed in previous structures[1].

Table 3.3 - Geometrical Data for Dithiocarbamate Ligands

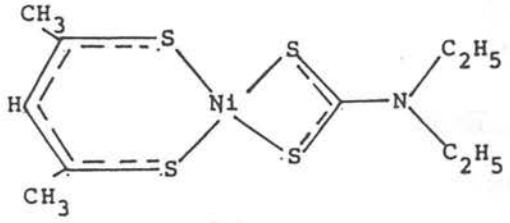
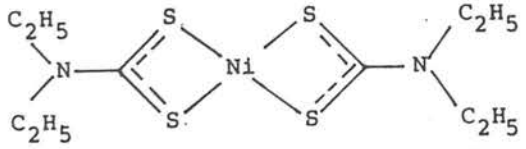
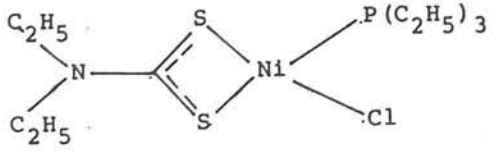
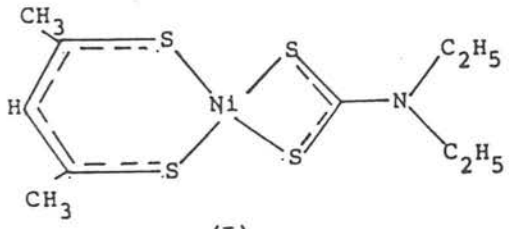
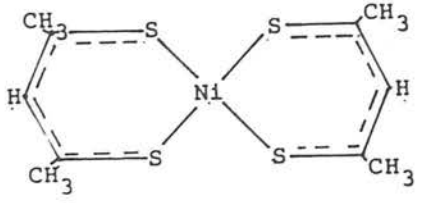
	Intra				
	Ni-S	S-Ni-S	S-C	N-C	S-C-S
 (I)	2.2246Å	78.1°	1.715Å	1.318Å	109.6°
 (II)	2.207 2.195	79.1	1.713 1.700	1.33	110.3
 (IV)	2.184(t-Cl) 2.241(t-PEt_3)	78.7	1.728 1.723	1.30	108.4

Table 3.4 - Geometrical Data for Dithio-Acetylacetonate Ligands



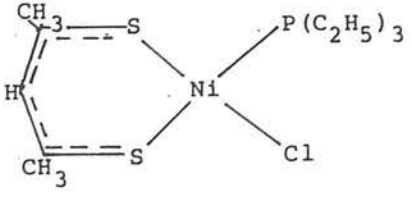
(I)

Ni-S	Intra S-Ni-S	Extra S-Ni-S	S-C	C-C	Ŝ(2)	Ĉ(1)	Ĉ(3)
2.1128Å	100.8°	90.6°	1.685Å	1.380Å	116.7°	127.6°	130.4°



(III)

2.156	97.2	82.8	1.685	1.381	118.1	128.4	128.7



(V)

2.108(t-Cl)	97.9		1.693	1.38	118.3	130.1	126.7
2.154(t-PEt_3)			1.705	1.39	117.9	128.2	

3.3 The Crystal and Molecular Structure of [(dithio-1,1,1-trifluoroacetylacetonato)(N,N-di-isopropyldithiocarbamato) nickel(II)], [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]

(a) Experimental

The compound [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)] (VI) was prepared as previously reported in Chapter 2. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation from a dichloromethane/60-80 petroleum ether mixture. A crystallographic study (conducted by Dr. A.J. Blake) on a flat needle crystal of dimensions 0.48 x 0.10 x 0.062mm identified the crystal as orthorhombic.

Crystal Data - $C_{12}H_8F_3NNiS_4$, M = 420.2, orthorhombic, space group P_{bca}, a = 23.007(16), b = 14.918(11), c = 10.761(10)A°, V = 3693A°^{3}, Z = 8, D_c = 1.511gcm^{-3}, MoKα radiation (λ = 0.71069 A°), μ = 15.08 cm^{-1}, T = 293K, R = 0.0813.

The fractional co-ordinates for all atoms are given in Table 3.5 Bond lengths and angles are shown in Table 3.6 and a drawing of the asymmetric molecule is presented in Figure 3.2.

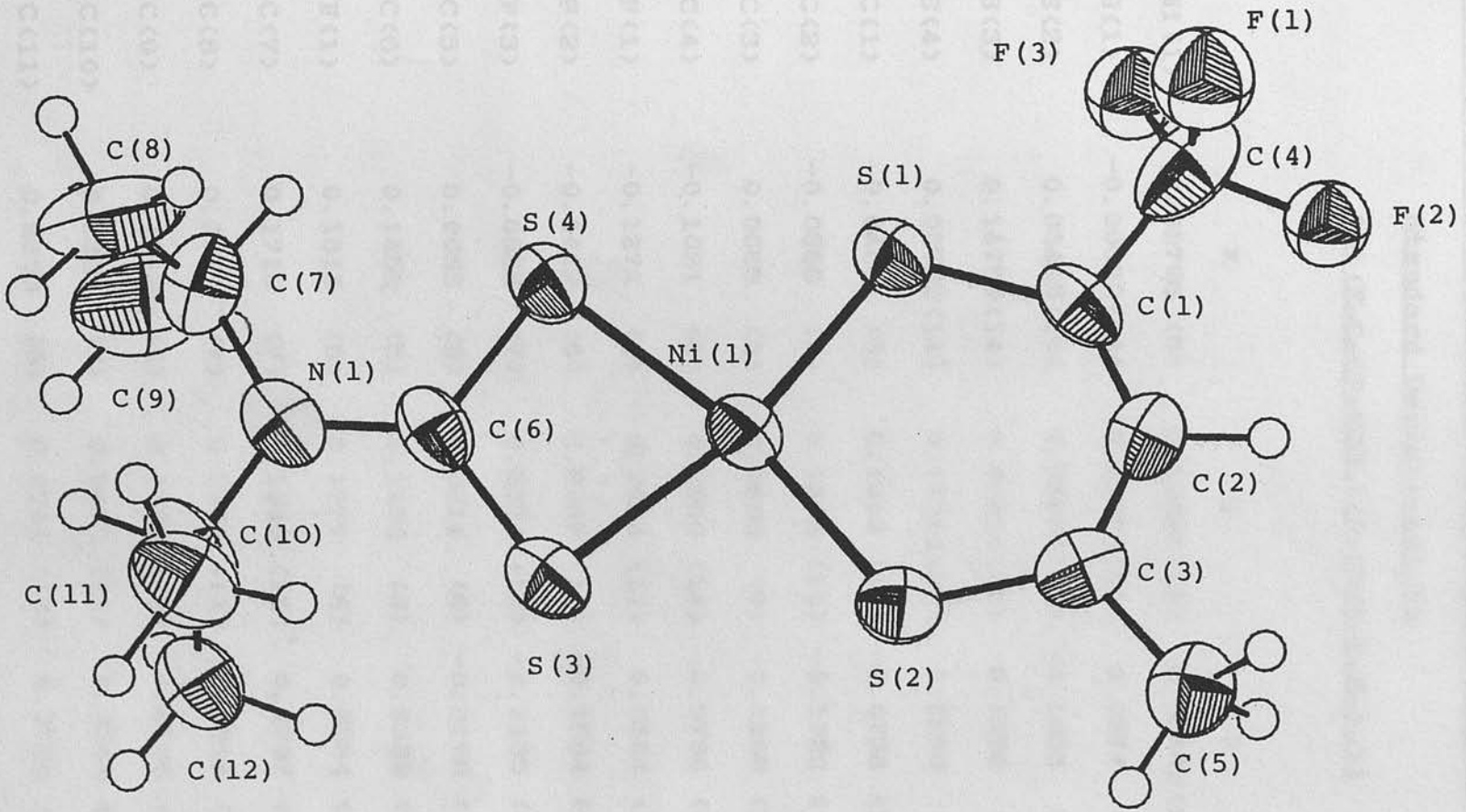


Figure 3.2 - $[Ni(S_2CN(i\text{-}C_3H_7)_2)(S_2C_3CF_3HCH_3)]$

Table 3.5 Fractional Co-ordinates of Atoms (with Standard Deviations) in [Ni($S_2C_2CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]

	x	y	z
Ni(1)	0.06796 (6)	0.12628(10)	0.06842(15)
S(1)	-0.00632(14)	0.20900(21)	0.0574 (4)
S(2)	0.06425(16)	0.05700(23)	-0.1038 (3)
S(3)	0.14750(14)	0.05226(25)	0.1238 (4)
S(4)	0.08709(14)	0.18311(24)	0.2550 (3)
C(1)	-0.0460 (5)	0.1942 (10)	-0.0738 (16)
C(2)	-0.0368 (6)	0.1388 (10)	-0.1722 (14)
C(3)	0.0085 (6)	0.0800 (9)	-0.1956 (14)
C(4)	-0.1031 (6)	0.2560 (14)	-0.0736 (19)
F(1)	-0.1271 (6)	0.2630 (11)	0.0344 (17)
F(2)	-0.1412 (6)	0.2247 (10)	-0.1584 (15)
F(3)	-0.0853 (7)	0.3371 (12)	-0.1135 (22)
C(5)	0.0053 (5)	0.0314 (8)	-0.3176 (14)
C(6)	0.1459 (5)	0.1130 (8)	0.2589 (14)
N(1)	0.1818 (5)	0.1077 (8)	0.3564 (14)
C(7)	0.1715 (7)	0.1640 (13)	0.4707 (17)
C(8)	0.2167 (7)	0.2268 (11)	0.4918 (17)
C(9)	0.1512 (8)	0.1105 (12)	0.5709 (18)
C(10)	0.2324 (7)	0.0485 (11)	0.3548 (18)
C(11)	0.2803 (6)	0.0761 (10)	0.2756 (15)
C(12)	0.2196 (6)	-0.0486 (9)	0.3580 (13)

Table 3.6 Bond Lengths (A°) and Bond Angles (°) in [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)]

Bond Lengths (A°)

Ni(1) - S(1)	2.111(4)	C(3) - C(5)	1.502(20)
Ni(1) - S(2)	2.124(4)	S(2) - C(3)	1.654(15)
Ni(1) - S(3)	2.219(4)	S(3) - C(6)	1.713(14)
Ni(1) - S(4)	2.224(4)	S(4) - C(6)	1.711(14)
S(1) - C(1)	1.696(15)	C(6) - N(1)	1.337(18)
C(1) - C(2)	1.359(21)	N(1) - C(7)	1.508(22)
C(2) - C(3)	1.385(21)	N(1) - C(10)	1.463(21)
C(1) - C(4)	1.606(25)	C(7) - C(8)	1.417(25)
C(4) - F(1)	1.29 (3)	C(7) - C(9)	1.421(26)
C(4) - F(2)	1.35 (3)	C(10)- C(11)	1.453(23)
C(4) - F(3)	1.35 (3)	C(10)- C(12)	1.479(22)

Bond Angles (°)

S(1) - Ni(1) - S(2)	101.71(15)
S(1) - Ni(1) - S(4)	89.31(14)
S(1) - Ni(1) - S(3)	166.78(15)
S(2) - Ni(1) - S(4)	168.98(15)
S(2) - Ni(1) - S(3)	91.46(14)
S(3) - Ni(1) - S(4)	77.52(14)
Ni(1) - S(1) - C(1)	114.0 (3)
Ni(1) - S(2) - C(3)	116.8 (5)

Ni(1) -	S(4) -	C(6)	86.9 (5)
Ni(1) -	S(3) -	C(6)	87.0 (5)
S(1) -	C(1) -	C(2)	130.1 (12)
C(1) -	C(2) -	C(3)	130.1 (14)
S(3) -	C(6) -	N(1)	128.4 (11)
S(4) -	C(6) -	N(1)	122.9 (10)
C(6) -	N(1) -	C(7)	120.7 (13)
C(6) -	N(1) -	C(10)	121.2 (13)
C(7) -	N(1) -	C(10)	118.0 (13)
N(1) -	C(7) -	C(8)	112.6 (15)
C(2) -	C(3) -	S(2)	127.3(12)
S(1) -	C(1) -	C(4)	111.4(11)
S(2) -	C(3) -	C(5)	117.4(10)
C(2) -	C(1) -	C(4)	118.6(14)
C(2) -	C(3) -	C(5)	115.3(13)
C(1) -	C(4) -	F(1)	113.5(16)
C(1) -	C(4) -	F(2)	109.4(15)
C(1) -	C(4) -	F(3)	105.5(16)
F(1) -	C(4) -	F(2)	111.0(18)
F(1) -	C(4) -	F(3)	110.2(18)
F(2) -	C(4) -	F(3)	107.0(18)
S(3) -	C(6) -	S(4)	108.6(7)
N(1) -	C(7) -	C(9)	111.0(15)
C(8) -	C(7) -	C(9)	119.4(16)
N(1) -	C(10)-	C(11)	116.1(14)
N(1) -	C(10)-	C(12)	115.6(13)
C(11)-	C(10)-	C(12)	116.3(14)

(b) Results and Discussion

(i) The Nickel Co-ordination Geometry:

The crystal is composed of discrete neutral molecules, (analogous to [Ni($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$)]), with the anticipated essentially planar but strongly asymmetric NiS_4 co-ordination. The molecule itself is not precisely planar, with a slight fold through S(1) and S(2) (but less significant than that found in [Ni(SacSac)$_2$]'), such that a dihedral angle of 2.0° occurs between the plane of best fit through S(1), Ni(1), S(2) and the plane of best fit through the ligand atoms S(1), C(1), C(2), C(3), S(2). This extent of folding is not repeated about S(3) - S(4) in the Ni($S_2CN(i-C_3H_7)_2$) moiety. Further measurements have shown the two ligand planes, defined by Ni(1), S(4), C(6), S(3) and Ni(1), S(1), C(1), C(2), C(3), S(2), to be inclined at 2.7°.

In this hybrid, the dtc Ni-S bonds are noticeably longer (ca. 2.22A°) than those found in Ni($S_2CN(i-C_3H_7)_2)_2$] (VII) (Ca. 2.18A°) and almost identical to the dtc Ni-S bond lengths discovered in hybrid I (2.225A°). The increase in the dtc Ni-S bond length in moving from VII to VI (0.04A°) over moving from II to I (0.022A), is explained by the unexpected short Ni-S bond lengths attributed to the [Ni($S_2CN(i-C_3H_7)_2)_2$] parent complex, which contrast with those found in [Ni($S_2CN(C_2H_5)_2)_2$] and

$[Ni(S_2CN(n\text{-}C_3H_7)_2)_2]$ (both ca. 2.20A°)[7,13]. Nevertheless, the dtc Ni-S bonds (in the hybrid) remain virtually identical, establishing that the inductive influence of the CF_3 substituent on the 1,3-dithiochelate is not localised in the 1,1-dithio-ring system (i.e. no observed augmentation of the <u>trans</u> effect).

As no crystallographic examination of the $[Ni(S_2C_3CF_3HCH_3)_2]$ complex has yet been reported, comparison of the hybrid 1,3-dithio Ni-S bond lengths with those found in the parent cannot be pursued. However, a comparison between the two hybrids (I and VI) reveals that the 1,3-dithio Ni-S bond lengths are closely similar, with the asymmetry found in the $[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$ hybrid, due to the CF_3 substituent restricted to ca. 0.01A° [Ni-S = 2.124A° (trans-CF_3) and 2.111A° (cis-CF_3)].

The intraligand S---S distances are 3.27A° (1,3-dithio) and 2.78A° (1,1-dithio), with interligand S---S distances of 3.11A° (S_2-S_3, see Figure 3.2) and 3.05A° (S_1-S_4). All these distances are less than the sum of sulphur van der Waals radii (3.48A°)[12] and permit the possibility of direct S---S electronic interaction. These S---S distances enforce a greater difference in S-Ni-S bite angles (i.e. 1,3-dithio = 101.7°; 1,1-dithio = 77.5°), than found previously in hybrid I.

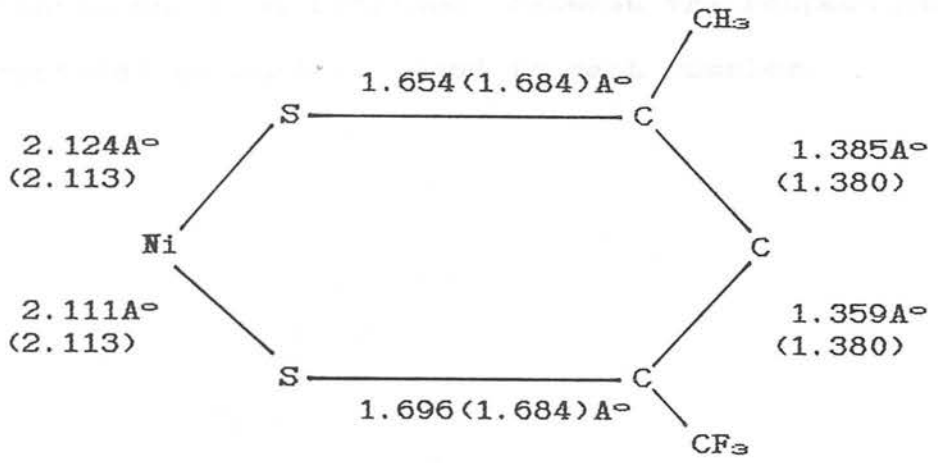
ii) Ligand Geometry (1,1-dithio-chelate):

In VI, steric interaction between the terminal iso-propyl substituents leads to the non-equivalence of these groups, resulting in the terminal methyl groups directed towards sulphur on one side of the ligand, and the hydrogen associated with the sulphur atom on the opposite side (as found in VII). The decrease in C-N and increase in S-C bond lengths discovered in going from II to I, associated with the increased importance of the $^{2-}S_2CNR_2^+$ canonical form, are surprisingly not enhanced in going from VII to VI. This suggests that the 1,1-dithio-ring geometry is rather insensitive to the anticipated variation in charge distribution, induced by the neighbouring stronger π-acceptor ligand ($S_2C_3CF_3HCH_3$). Relevant bond lengths and angles for VI, VII and I are compared in Table 3.7.

iii) Ligand Geometry (1,3-dithio-chelate)

Relevant data between hybrids VI and I are compared in Table 3.8. Strikingly, the influence of the CF_3 substituent is delocalised over the six-membered metallo-chelate ring. This produces an alternate increase and decrease in bond lengths within the ligand (in comparison to hybrid I), such that a bond that is shortened is bound by two longer bonds and vice-versa. These bond length

alterations are shown below, with the corresponding bond lengths found in I presented in parenthesis.



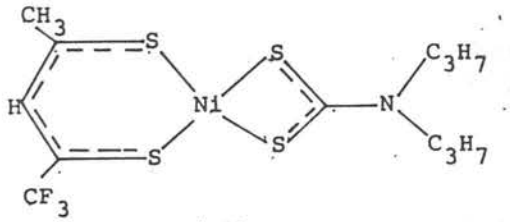
The internal angles of the 1,3-dithio-chelate are largely unaltered from those observed in I, with the exception of those angles directly affected by the CF_3 substituent. This stronger electron-withdrawing substituent leads to an increase in S(1)-C(1)-C(2) by 2.5A°, which is compensated by the reduction of 2.8A° in Ni(1)-S(2)-C(3).

This initial study of the Ni($S_2C_3CF_3HCH_3$) moiety in [Ni($S_2C_3CF_3HCH_3$)($S_2CN(i\text{-}C_3H_7)_2$)], shows that in principle the other 1,3-dithio-β-diketonate ligands, which have not yet been crystallographically examined, can be readily studied for the first time in a hybrid environment. For example, our preliminary X-ray study of [Ni(S_2C_3PhHPh)($S_2CN(i\text{-}C_3H_7)_2$)][14], has determined, for the first time, that the two phenyl substituents do not lie in the same plane, in addition to being twisted out of the plane of the 1,3-dithio-β-diketonate ring.

Therefore, complete X-ray structural analyses of a hybrid series [M(S_2C_3RHR')($S_2CNR''_2$)] (for constant M, R'' and R,R' = CH_3, CF_3, Ph) would enable effective comparisons to be obtained, between the respective structural parameters found in each complex.

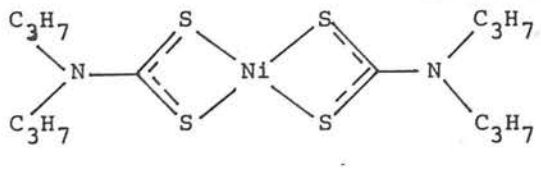
Table 3.7 - Geometric Data for Dithiocarbamate Ligand

	Intra			
Ni-S	S-Ni-S	S-C	N-C	S-C-S
2.219 Å	77.5°	1.713 Å	1.337 Å	108.6°
(trans CF_3)		(trans CF_3)		
2.224		1.711		
(cis CF_3)		(cis CF_3)		



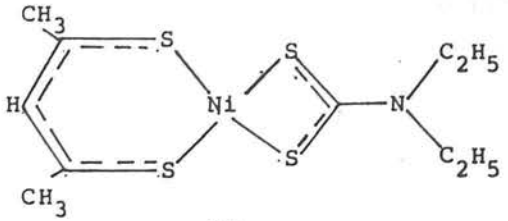
(VI)

2.183	79.6	1.711	1.329	109.2
2.182		1.714		
2.181	78.9	1.673	1.337	109.5
2.179		1.720		



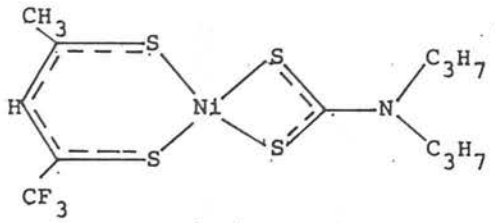
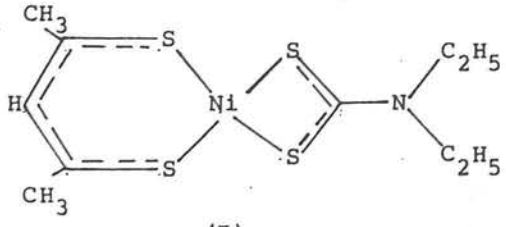
(VII)

2.2246	78.1	1.715	1.318	109.6



(I)

Table 3.8 - Geometric Data for Dithio-β-Diketonates in Hybrid Complexes

	Intra Ni-S	extra S-Ni-S	S-Ni-S	S-C	C-C	$\hat{S}$	$\hat{C}$	$\hat{C}(2)$
 (VI)	2.111 Å	101.7°	89.3°	1.696 Å	1.359 Å	114.0°	130.1°	130.1°
	(cis CF_3)			(S(1)-C(1))	(C(1)-C(2))	(S(1))	(C(1))	
	2.124		91.5	1.654	1.385	116.8	127.3	
	(trans CF_3)			(S(2)-C(3))	(C(2)-C(3))	(S(2))	(C(3))	
 (I)	2.1128	100.8	90.6	1.68	1.380	116.7	127.6	130.4

Chapter 3 - References

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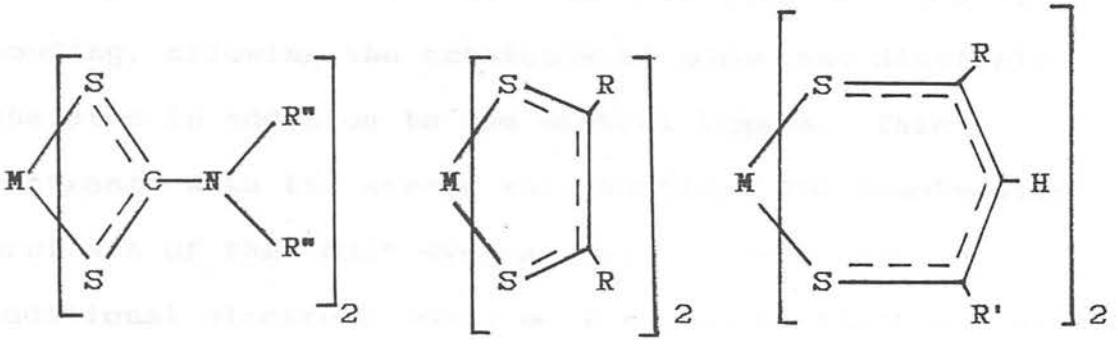
CHAPTER 4

Electrochemical Studies of Nickel, Palladium and Platinum 1,1-Dithio-1,3-Dithio-Hybrid Complexes

4.1 Introduction

(a) Theoretical and Experimental Assignments of [M(S_2C_3RHR')$_2$] Reductions



(I) (II) (III)

The interpretation of the two successive one-electron transfers observed in the complexes [M(S_2C_3RHR')$_2$] (III), with respect to ligand-orbital or metal-orbital participation was initially tentative due to conflicting theoretical predictions, previously introduced by Schrauzer[1] and McCleverty[2] (Chapter 1), combined with the lack of sufficient experimental data. McCleverty proposed that the planar delocalised 1,3-dithio-β-diketonates (III) would show similar reversible ligand-centred one-electron transfers, to those discovered in the dithiolenes (II). Schrauzer however drew attention to the topological distinction between "odd" (1,1-dithio and 1,3-dithio) and "even" (1,2-dithio) resonance-stabilized ligands and conversely predicted that the remarkable redox properties

discovered in the "even" systems would not be shared with those of the "odd" complexes.

In studying the schematic Π-molecular orbital diagrams for the "odd" and "even" dithio ligands (see Figure 4.1), Schrauzer concluded that the "even" systems have a lowest unoccupied orbital available that is only weakly anti-bonding, allowing the existence of mono- and dianionic chelates in addition to the neutral ligand. This contrasts with the strong anti-bonding LUMO Π-molecular orbitals of the "odd" systems, which imply that no additional electrons would be accepted by these 1,1-dithio- and 1,3-dithiochelates beyond the radical monoanion.

Since the 1,3-dithio-ligand should be non-reducible, the application of this "odd-even" criterion would attribute the two polarographically observed reductions[3] of $[M(S_2C_3CH_3HCH_3)_2]$ to successive M^{II}/M^{I} and M^{I}/M^{0} valency changes. In contrast, advanced molecular orbital calculations for both $[M(S_2C_2H_2)_2]$ and $[M(S_2C_3H_3)_2]$ systems have indicated dominant ligand character in the respective redox-active orbitals[4].

Subsequent experimental evidence also strongly supports the assignment of the 1,3-dithio-β-diketonate reductions as ligand-centred. Reduction potential/Substituent effect correlations for the $[Ni(S_2C_3RHR')_2]$ systems by Hendrickson and co-workers[5] and further studies by Bowden, Holloway and Geiger[6], both show linear plots, indicating orderly variations in E° red(1) with differing substituents for the electron-transfer

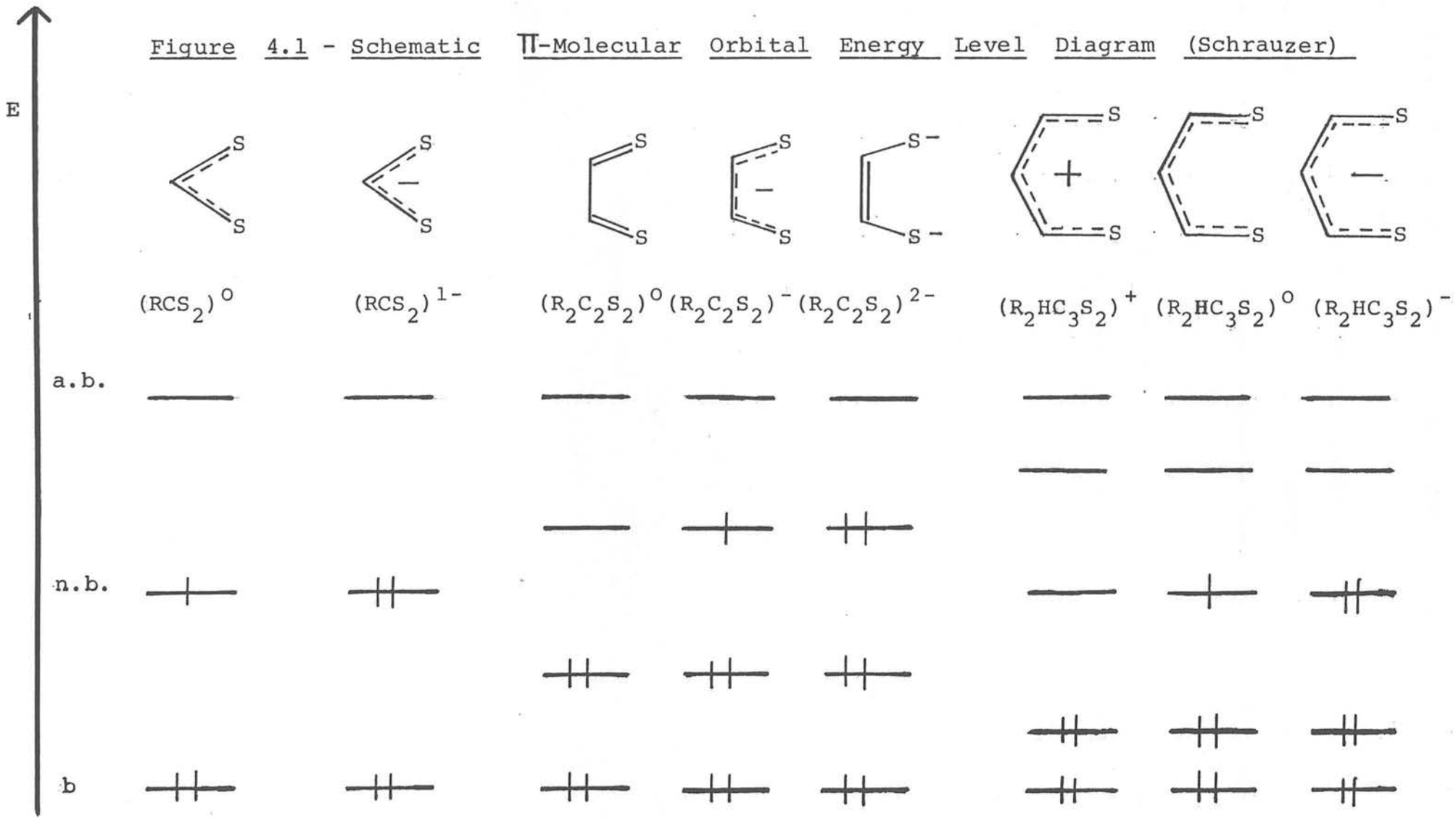


Figure 4.1 - Schematic π-Molecular Orbital Energy Level Diagram (Schrauzer)
E
$(RCS_2)^0$
$(RCS_2)^{1-}$
$(R_2C_2S_2)^0$
$(R_2C_2S_2)^-$
$(R_2C_2S_2)^{2-}$
$(R_2HC_3S_2)^+$
$(R_2HC_3S_2)^0$
$(R_2HC_3S_2)^-$
a.b.
n.b.
b

process $[Ni(S_2C_3RHR')_2]^{0/1-}$, consistent with ligand-orbital participation.

The range of available Pd and Pt- centred bis-1,3-dithio-β-diketonates has recently been extended by Heath and Leslie[7]. Importantly, these systems reveal that the positions of the first and second reductions for a particular ligand are virtually identical, independent of the central metal ion (Ni,Pd,Pt). The last observation is essential in establishing ligand participation, as the metal-based ($Ru^{III/II}$) reductions of $[Ru(O_2C_3RHR')_3]$ also exhibit linear E^o vs. ligand substituent Hammett inductive parameter plots[8], comparable to those reported for $[Ni(S_2C_3RHR')_2]^{0/1-}$. Heath and Leslie have also compared Reduction potential/Substituent effect correlations for $[M(S_2C_3RHR')_2]^{0/1-}$ (odd) and $[M(S_2C_2R_2)_2]^{0/1-}$ (even) processes. The closely similar respective gradients once again support ligand-based redox activity in both species.

Spectroscopic confirmation of the ligand-centred nature of the reductions in the $[M(S_2C_3RHR')_2]$ systems (M=Ni,Pd,Pt) was eventually achieved by recent low temperature esr studies completed by Bowmaker and co-workers[9] on the electrogenerated radical anions arising from the first reductions of $[Ni(SacSac)_2]$ and $[Pd(SacSac)_2]$. There is still room for doubt as to whether the unpaired electron is delocalised over both the mutually coplanar ligands as assumed[9] or restricted to one.

Therefore Schrauzers' "odd-even" criterion requires re-examination since it was taken to mean that the LUMO in $[M(S_2C_3RHR')_2]$ was too strongly anti-bonding to accept additional electrons beyond the monoanion $(S_2C_3RHR')^-$. The $[M(S_2C_3RHR')_2]$ acceptor orbital in fact lies at higher energy than that found in the LUMO of $[M(S_2C_2R_2)_2]$ (by almost 0.8 eV), but this leads to relatively negative reversible reduction potentials in the metal bis-1,3-dithio-β-diketonates, rather than the predicted absence of ligand-mediated electron-transfer activity.

The main purpose of this chapter is to describe and interpret the electrochemical behaviour of the hybrid 1,1-1,3- dithio complexes $[M(S_2CNR"_2)(S_2C_3RHR')]$. According to the introductory analysis above, these may be expected to contain one non-reducible (1,1-dithio) and one reducible (1,3-dithio) ligand. Thus the hybrid complexes are almost structurally isomeric with the "even" bis-1,2-dithio systems $[M(S_2C_2R_2)_2]$, but should have very different properties.

In the following sections, the description of the electrochemical behaviour of the hybrid systems (Section 4.2) is preceded by a review of the important voltammetric characteristics of $[M(S_2C_3RHR')_2]$ (Section 4.1(b)) and $[M(S_2CNR"_2)_2]$ (Section 4.1 (c)). This turns out to provide a helpful basis for discussion.

(b) Voltammetry of $[M(S_2C_3RHR')_2]$ Complexes

Cathodic electrochemical investigations concerning the parent complexes $[M(SacSac)_2]$ (M=Ni,Pd,Pt) have established competing respective E_1E_2 and E_1CE_3 reductive pathways (Scheme 4.1) through a.c., d.c. and cyclic voltammetric analyses.

Scheme 4.1

$$[M(SacSac)_2] \underset{E_1}{\overset{a}{\rightleftharpoons}} [M(SacSac)_2]^{1-} \underset{E_2}{\overset{b}{\rightleftharpoons}} [M(SacSac)_2]^{2-}$$

$$\text{"Rearrangement"} \quad k \downarrow$$

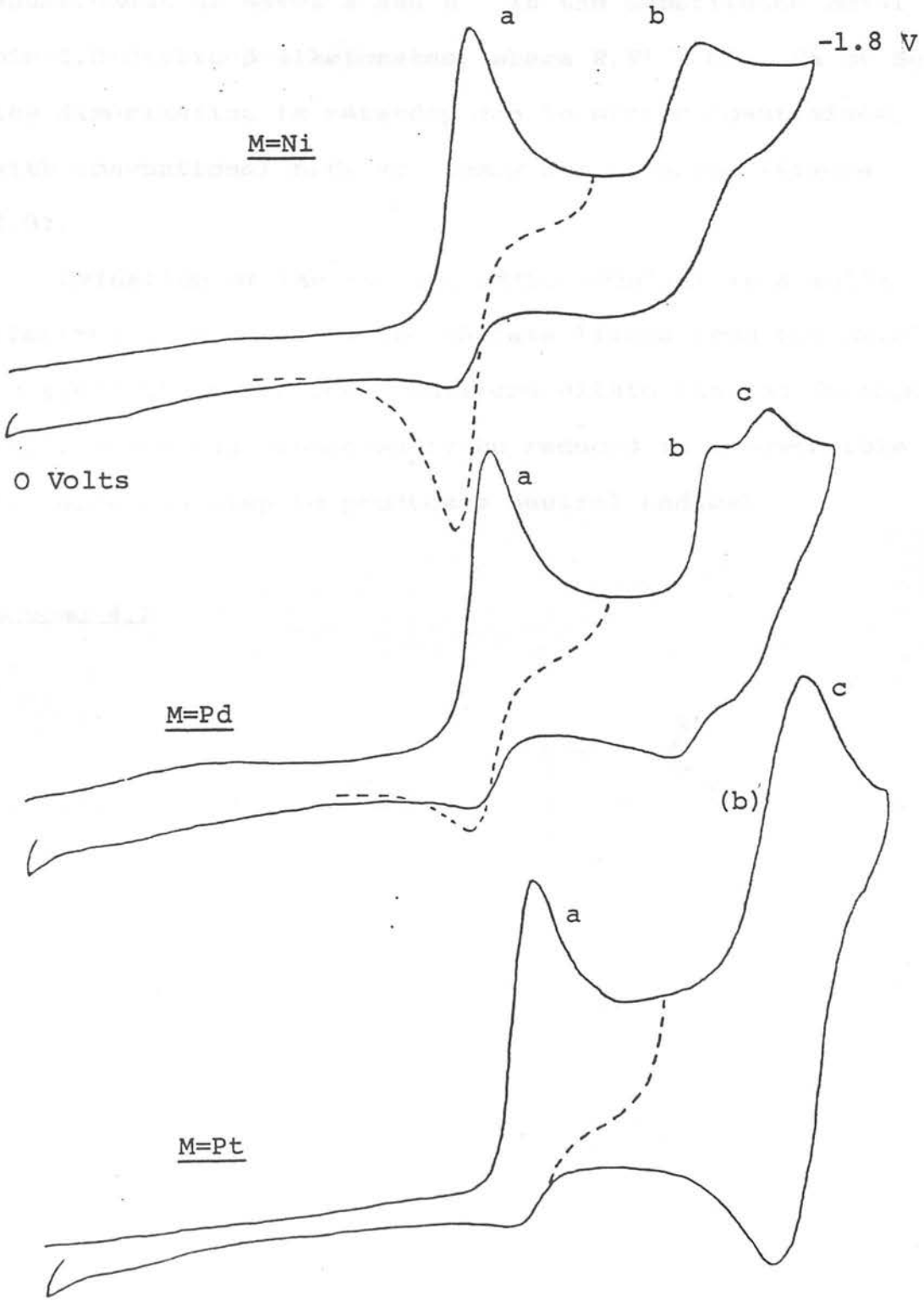
$$[\{M(SacSac)_2\}_2]^{2-} \underset{E_3}{\overset{c}{\rightleftharpoons}} [\{M(SacSac)_2\}_2]^{4-}$$

These competing pathways are shown in Figure 4.2, which exhibits the voltammetry of the two $[M(SacSac)_2]$ (M=Ni,Pd,Pt) reductions.

The rearrangement was initially noted in polarographic studies of $[M(SacSac)_2]$ by Bond, Heath and Martin in 1970[3]. Geiger proposed that a dimeric radical anion was formed in the chemical step of the E_1CE_3 mechanism[6]. Kinetic studies by Heath and Leslie have positively identified the identity of the rearrangement as a dimerisation[3,10].

The rate constant for the dimerisation process increases in the order Ni<<Pd<Pt, with the $[Pt(SacSac)_2]$

Figure 4.2 - Cyclic Voltammograms of $M(SacSac)_2$ Complexes (M=Ni,Pd,Pt).



voltammogram dominated by this pathway (i.e. path c dominates over path b). Unlike the Pd and Pt systems, [Ni(SacSac)$_2$] shows little sign of rearrangement at ambient temperature, whereas faster scan-rates or lower temperatures are required to suppress the dimerisation in both [Pd(SacSac)$_2$] and [Pt(SacSac)$_2$], resulting in the enhancement of waves a and b. In the substituted metal bis-1,3-dithio-β-diketonates, where R,R' = CF_3, Ph or Bu^t, the dimerisation is retarded due to steric constraints, with conventional E_1E_2 voltammograms observed (Figure 4.3).

Oxidation of the systems [M(S_2C_3RHR')$_2$] in a multi-electron step, cleaves the chelate ligand from the metal to yield the resonance-stabilised dithiolium ion (Scheme 4.2), which can subsequently be reduced in a reversible one-electron step to produce a neutral radical.

Scheme 4.2

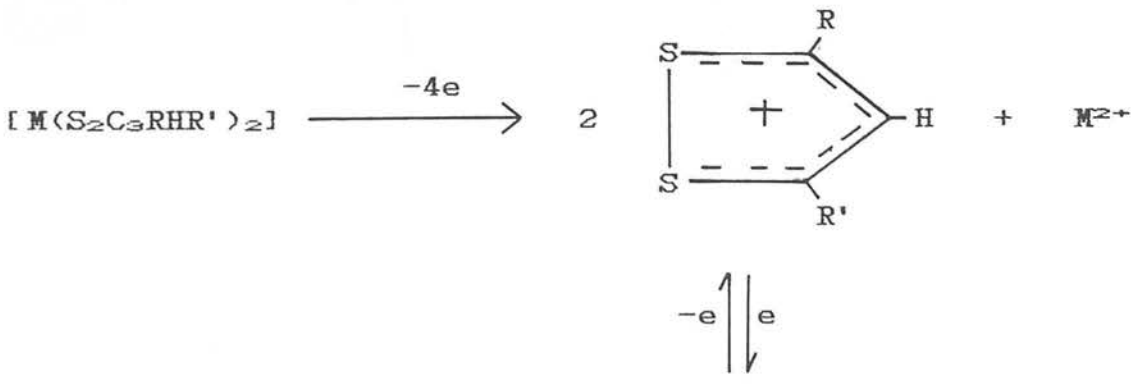
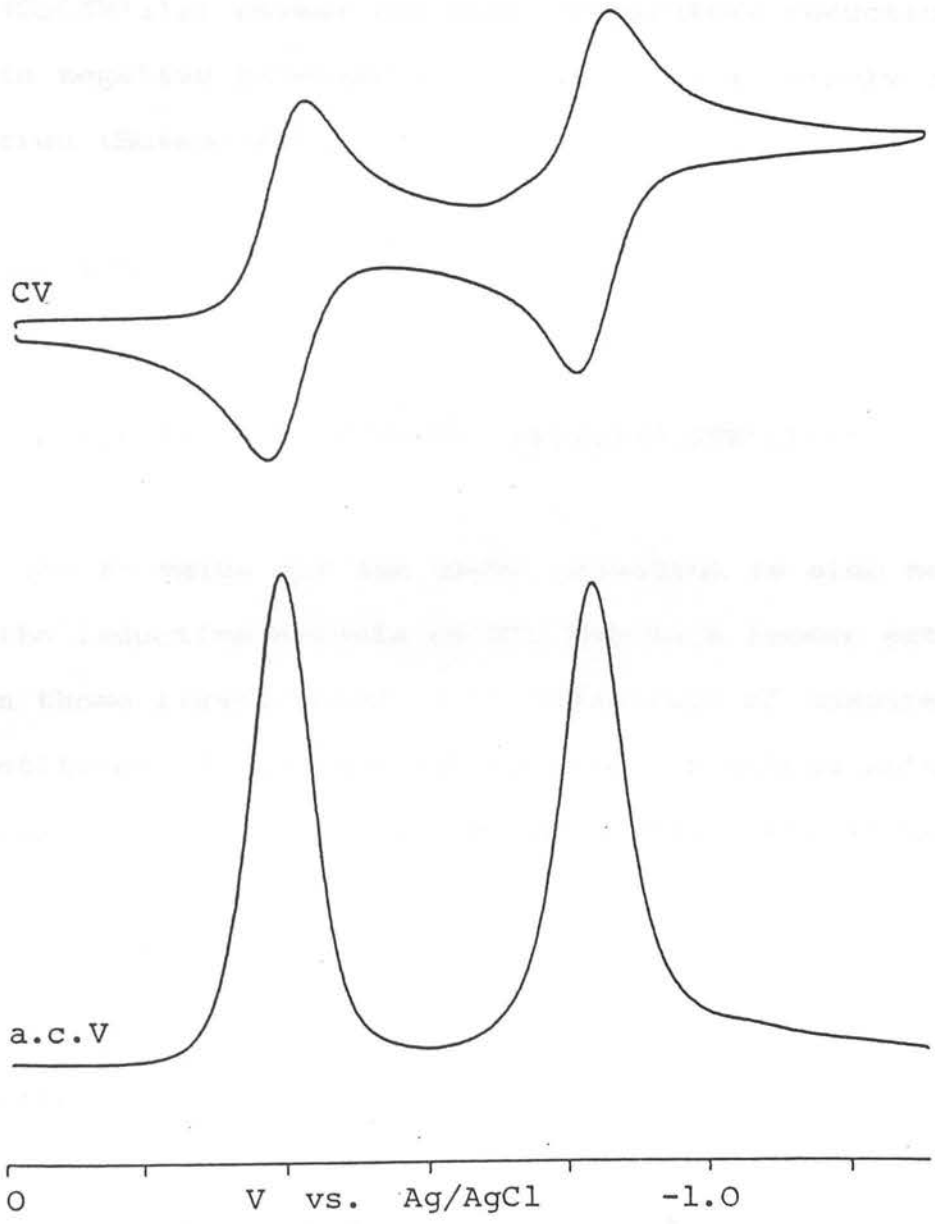


Figure 4.3 - Voltammetry of $[Pd(S_2C_3CF_3HCH_3)_2]$ in Dichloromethane.



(c) Voltammetry of $[M(S_2CNR''_2)_2]$ Systems

As previously mentioned, these 1,1-dithio-complexes exhibit contrasting electrochemical behaviour with that found in the metal bis-1,3-dithio-β-diketonates. Remarkably, the nickel-centred systems produce a series of complexes which display all formal nickel oxidation states from I to IV[11].

Extensive studies for the neutral compounds $[Ni(S_2CNR''_2)_2]$ reveal one quasi-reversible reduction at quite negative potentials[11,12] which is genuinely metal-centred (Scheme 4.3).

Scheme 4.3

$$[Ni(II)(S_2CNR''_2)_2] \rightleftharpoons^{e^-} [Ni(I)(S_2CNR''_2)_2]^-$$

The E^o value for the above reduction is also sensitive to the inductive effects of R", but to a lesser extent than those ligand-based first reductions of comparably substituted $[Ni(S_2C_3RHR')_2]$ systems. Electron spin-resonance examinations of the mono-anion radical have identified the predominant metal character in the redox-active orbital[13].

The electrochemistry of the nickel bis-dialkyldithiocarbamates[11,14,15] is very complex, particularly in the anodic range, with Schemes 4.4(a) - 4.4(c) determined by Hendrickson, Martin and Rhode[11].

Scheme 4.4(a) (mechanism unknown)

$$3[Ni^{II}(S_2CNR''_2)_2] \xrightarrow{-4e} 2[Ni^{IV}(S_2CNR''_2)_3]^+ + Ni^{2+}$$

Scheme 4.4(b)i

$$[Ni^{IV}(S_2CNR''_2)_3]^+ \overset{e}{\rightleftharpoons} [Ni^{III}(S_2CNR''_2)_3]$$

Scheme 4.4(b)ii

$$[Ni^{III}(S_2CNR''_2)_3] \overset{e}{\rightleftharpoons} [Ni^{II}(S_2CNR''_2)_3]^-$$

$$\downarrow \qquad\qquad \downarrow$$

$$[Ni^{II}(S_2CNR''_2)_2] \qquad [Ni^{II}(S_2CNR''_2)_2]$$

$$+ \qquad\qquad +$$

$$\tfrac{1}{2}[R_2NCS_2\text{-}S_2CNR_2] \xleftarrow{-e} ((S_2CNR''_2)^- \ *$$

(* $(S_2CNR''_2)^-$ detected through its oxidation by cyclic voltammetry[20])

Scheme 4.4(c)

$$[Ni^{IV}(S_2CNR''_2)_3]^+ + (S_2CNR''_2)^- \longrightarrow [Ni^{II}(S_2CNR''_2)_2] + [R_2NCS_2\text{-}S_2CNR_2]$$

Similar studies of palladium and platinum bis-dialkyldithiocarbamates by Van der Linden and Dix[16,17] have established that the palladium systems exhibit quasi-reversible cathodic behaviour analogous with that discovered in the nickel systems (Scheme 4.3). For $[Pt(S_2CNR''_2)_2]$, the reductions are wholly irreversible[17] with ligand expulsion, and extremely negative E^o values

(beyond -2.0V vs. Ag/AgCl) preclude detailed assignment. However, the large shifts between the reduction potentials of congeneric palladium and platinum complexes (-1.5V Pd and -2.0V Pt) tend to support metal-orbital participation.

Oxidation of the neutral complexes $[M(S_2CNR''_2)_2]$ (M = Pd,Pt) reveal ligand-transfer again, as in 4.4(a), to form tris-M(IV) compounds[17] ($[M^{IV}(S_2CNR''_2)_3]^+$). Both M(IV) species are very unstable and rapidly decompose in solution, particularly the cation $[Pd^{IV}(S_2CNR''_2)_3]^+$ which immediately gives $[Pd(S_2CNR''_2)_2]$. The greater stability of the Pt^{IV} cationic complexes have enabled a comprehensive analysis of their reduction processes[17], as set out in Schemes 4.5(a) - 4.5(b) below.

Scheme 4.5(a) (Presumed Course)

$$3[Pt^{II}(S_2CNR''_2)_2] \xrightarrow{-4e} 2[Pt^{IV}(S_2CNR''_2)_3]^+ + Pt^{2+}$$

$$[Pt^{IV}(S_2CNR''_2)_3]^+ \xrightarrow{2e} [Pt^{II}(S_2CNR''_2)_3]^-$$

$$[Pt^{II}(S_2CNR''_2)_3]^- \rightsquigarrow [Pt^{II}(S_2CNR''_2)_2] + (S_2CNR''_2)^- (*)$$

(* Detected by cyclic voltammetry)

Therefore, parallel metal-based (M^{II}/M^{I}) cathodic behaviour is probably followed by all d^8-metal bis-dialkyldithiocarbamates $[M(S_2CNR''_2)_2]$ (M=Ni,Pd,Pt), as in

4.3. In the anodic range, comparison of Schemes 4.4(b) and 4.5(b) reveals a greater stability for Ni^{III} than Pt^{III} (and presumably Pd^{III}), since oxidation state III is detected only in the nickel systems.

Consideration of the contrasting electrode processes discovered in the parent systems $[M(S_2C_3RHR')_2]$ and $[M(S_2CNR''_2)_2]$ suggested that three distinct cathodic electrochemical pathways were open to the $[M(S_2C_3RHR')(S_2CNR''_2)]$ hybrids:-

i) Reduction of the (S_2C_3RHR') ligand.

ii) A M^{II}/M^{I} reduction of the metal centre.

iii) Two reductions, involving firstly the 1,3-dithiochelate, followed by a more difficult M^{II}/M^{I} reduction (more negative E° value).

The anodic electrochemical behaviour of the hybrids was rather more difficult to predict but metal-centred oxidation, dithiocarbamate oxidation to the thiuram disulphide, or dithio-β-diketonate oxidation to the dithiolium heterocycle are the recognisable alternatives. In fact the latter seems to occur but the oxidations are experimentally considerably obscurred by electrode-coating.

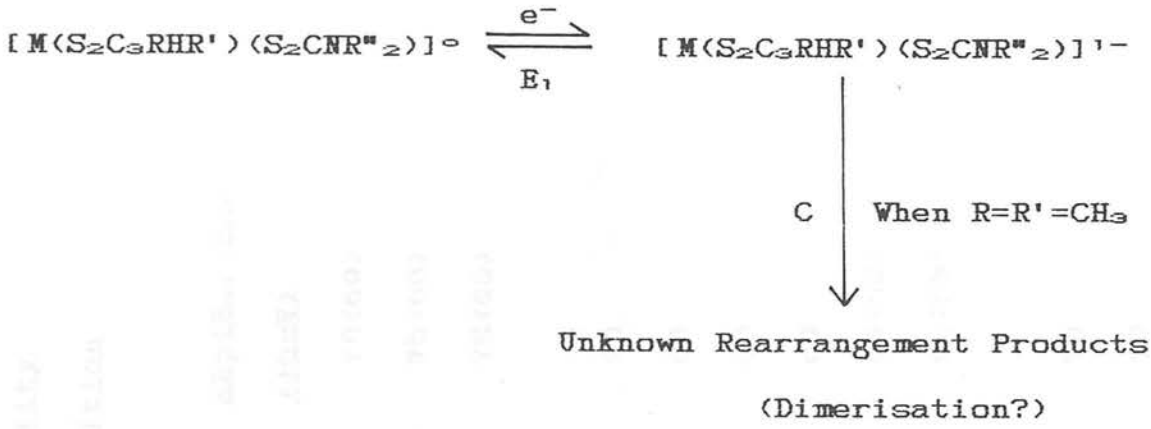
4.2 Electrochemical Studies of [M($S_2CNR"_2$)(S_2C_3RHR')] Hybrids

(a) Cathodic Investigations

The 1,1-dithio-1,3-dithio hybrid complexes all exhibit a solitary accessible reduction, which is fully reversible and corresponds to a one-electron reduction of the single 1,3-dithio-β-diketonate ligand. Charge donation from the dithiocarbamate to the 1,3-dithiochelate (as described in Chapter 2) causes the hybrid reduction to occur at more negative potentials than those observed for the corresponding process in the parent $[M(S_2C_3RHR')_2]^{0/1-}$, by approximately 200 - 300 mV.

The distinction between the kinetically controlled electrochemical behaviour of the parent compounds $[M(SacSac)_2]$ (E_1E_2 and E_1CE_3) and the $[M(S_2C_3RHR')_2]$ systems with bulkier substituents (simply E_1E_2) is mirrored in the hybrid systems, where the E_1C mechanisms exhibited by the [M(SacSac)($S_2CNR"_2$)] complexes are absent in those hybrids with bulkier substitution of the 1,3-dithio-ligand. These latter systems display greater reversibility and follow the simpler E_1 path, at least on the voltammetric timescale. Scheme 4.6, below, summarises the competing pathways found in the hybrid systems.

Scheme 4.6



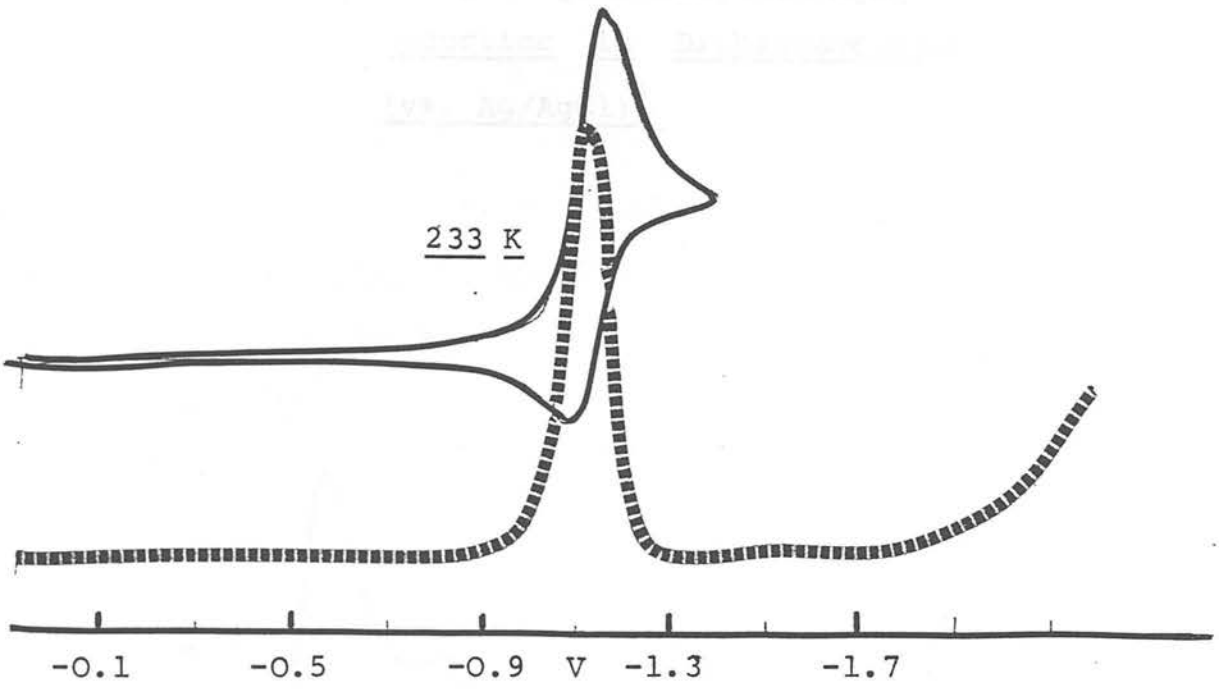
The partial irreversibility of the [M(SacSac)($S_2CNR"_2$)] systems (shown in i_{pr}/i_{pf} ratios ranging from 0.65-0.9) becomes more pronounced in the central ion sequence Pd>Pt>Ni, differing from the order of dimerisation rate constants for $[M(SacSac)_2]^{1-}$, which is Pt>Pd>>Ni [10]. Further electrochemical kinetic studies may help to identify the nature of the rearrangement that occurs in the transient radical monoanion $[M(SacSac)(S_2CNR"_2)]^{1-}$.

Reversibility comparisons for the hybrids, using classical cyclic voltammetric criteria (Table 4.6), are presented in Table 4.1. Faster scan-rates and lower temperatures reduce the extent of rearrangement in the $[M(SacSac)(S_2CNR"_2)]^{1-}$ species. Figures 4.4 and 4.5 demonstrate the reversibility enhancements of the $[M(SacSac)(S_2CN(C_2H_5)_2)]^{0/1-}$ electron-transfers (M=Pd,Pt) on lowering the temperature from 290K to 233K.

Table 4.1 Application of Cyclic Voltammetric Reversibility Criteria to $[M(S_2C_3RHR')(S_2CNR''_2)]^{0/1-}$ Transition

Complex				Temperature(K)	i_{pr}/i_{pf} (±0.05)	$\Delta Ep(E_{pf}-E_{pr})$ (±5mV)
M	R"	R	R'			
Ni	C_2H_5	CH_3	CH_3	290(230)	0.91(1.0)	70(60)
Pd	C_2H_5	CH_3	CH_3	290(233)	0.65(0.87)	75(60)
Pt	C_2H_5	CH_3	CH_3	290(231)	0.80(0.91)	75(60)
Ni	i-C_3H_7	CH_3	CH_3	290	0.87	70
Ni	i-C_3H_7	Ph	CH_3	290	1.0	60
Ni	i-C_3H_7	Ph	Ph	290	1.0	60
Ni	C_3H_7	CF_3	CH_3	290	1.0	60
Pd	C_2H_5	CF_3	CH_3	290(238)	0.87(0.95)	65(60)
Pt	C_2H_5	CF_3	CH_3	290(223)	0.90(1.0)	60(55)
Pt	C_4H_9	CH_3	CH_3	290	0.77	75
Ni	CH_3	CH_3	CH_3	290	0.90	70

Figure 4.4 - A.c. and CV Temperature Dependence of $[Pd(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]^{0/1-}$ Reduction in CH_2Cl_2 (vs. Ag/AgCl).



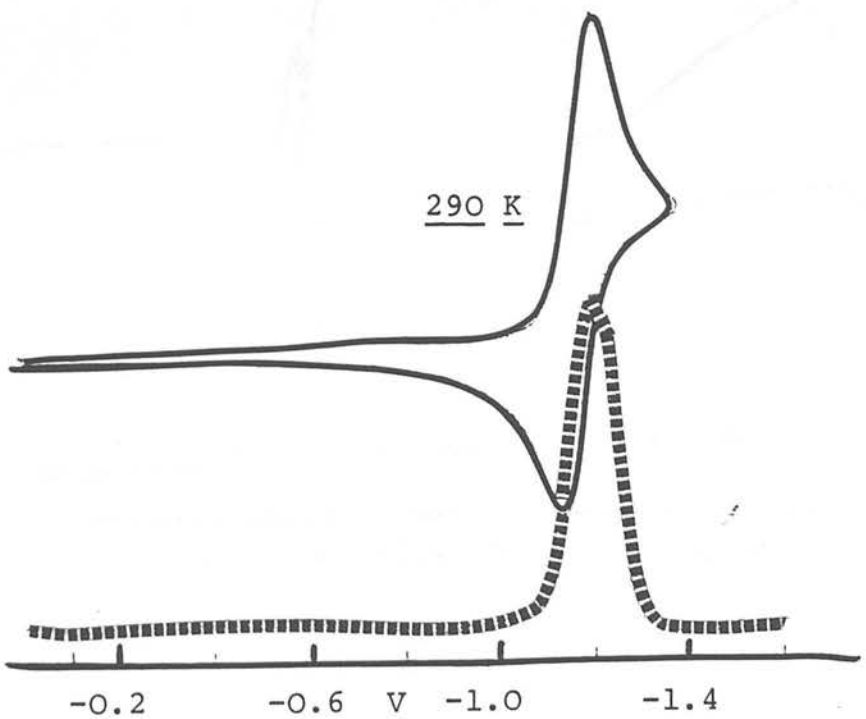
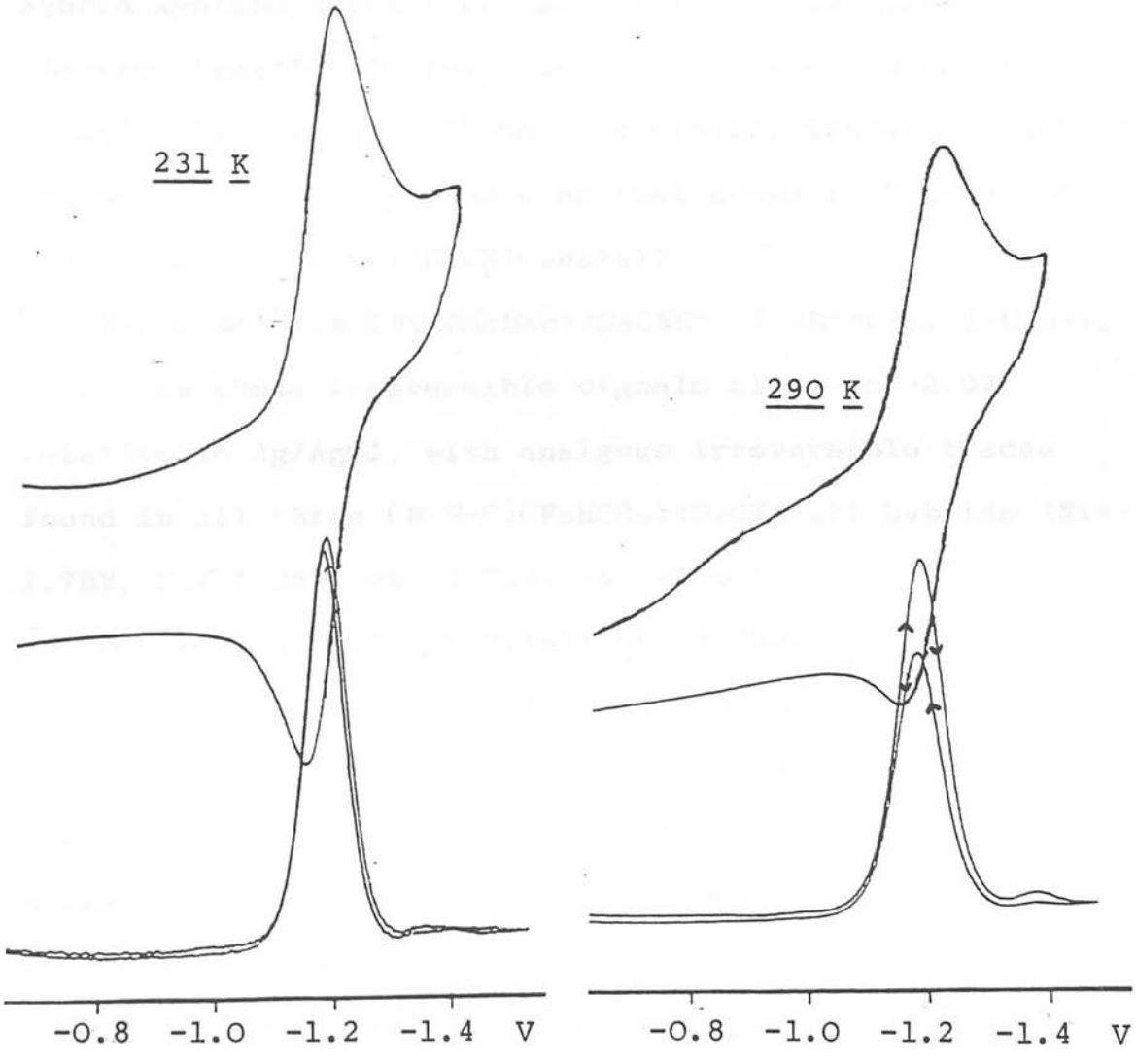


Figure 4.5 - A.c. and Cyclic Voltammetric Temperature Dependence of $[Pt(S_2C_3CH_3HCH_3)(S_2CN(C_2H_5)_2)]^{0/1-}$ Reduction in Dichloromethane (vs. Ag/AgCl).



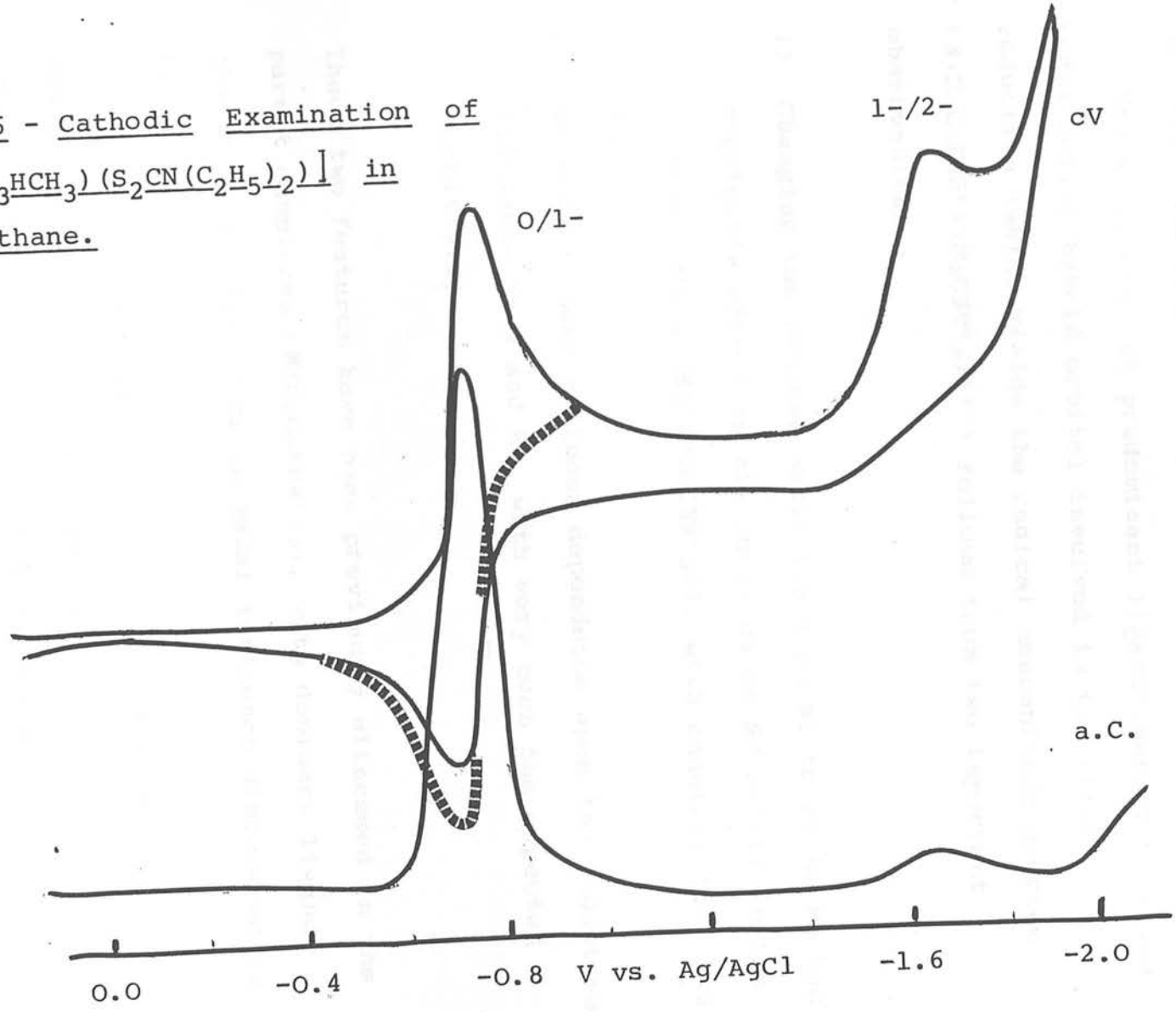
The nickel systems [Ni(S$_2$C$_3$RHR')(S$_2$CN(i-C$_3$H$_7$)$_2$)] (R,R'=CH$_3$,Ph; Ph,Ph; CF$_3$,CH$_3$ and CF$_3$,Ph) all exhibit near-classical cyclic voltammetric criteria at ambient temperatures, with no apparent sign of any monoanion rearrangement. The systems [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)] (M=Pd,Pt) exhibit slightly low i_{pr}/i_{pf} ratios of 0.90 at ambient temperatures but once again show increased i_{pr}/i_{pf} ratios at lower temperatures and faster scan-rates.

Although all the hybrid systems display one well-behaved reversible reduction, at modest E^o values, certain hybrid systems exhibit one additional irreversible electron-transfer in both the C.V. and a.c. modes, at more negative potentials. These irreversible traces are all of the same general appearance as that shown in Figure 4.6 for [Pt(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CN(C$_2$H$_5$)$_2$)].

The complexes [Ni(SacSac)(S$_2$CNR"$_2$)] (R"=CH$_3$, i-C$_3$H$_7$), both show these irreversible signals close to -2.0V, relative to Ag/AgCl, with analgous irreversible traces found in all three [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CNR"$_2$)] hybrids (Ni=-1.78V, Pd=-1.36V, Pt=-1.73V) and also in [Ni(S$_2$C$_3$PhHPh)(S$_2$CN(i-C$_3$H$_7$)$_2$)] at -1.63V.

The similarity in the E^o values of the later irreversible reductions for the nickel and platinum-centred [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CNR"$_2$)]$^-$ hybrid monoanions, suggest that the reduction is once again ligand-based. Therefore, at this early stage, the likely product of the reduction appears to be [M^{II}(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$CNR"$_2$)]$^{2-}$, with the electron either completing the half-filled weakly

Figure 4.6 - Cathodic Examination of $[Pt(S_2C_3CF_3HCH_3)(S_2CN(C_2H_5)_2)]$ in Dichloromethane.



anti-bonding orbital of the 1,3-dithio-β-diketonate or entering the anti-bonding orbital of the dialkyldithiocarbamate ligand (previously unaccessible in the parent $[M(S_2CNR"_2)_2]$ systems).

The assignment of predominant ligand-character to the redox-active hybrid orbital involved in the first reduction (which yields the radical monoanionic species $[M(S_2C_3RHR')(S_2CNR"_2)]^{1-}$) follows from two important observations:-

1) Changing the central metal ion from Ni to Pd to Pt has negligible effect on the position of E^o red(1) in the systems $[M(S_2C_3RHR')(S_2CNR"_2)]$, with constant R, R' and R".
2) E^o red(1) shows a linear dependence upon the inductive influence of R and R', with very much the expected sensitivity.

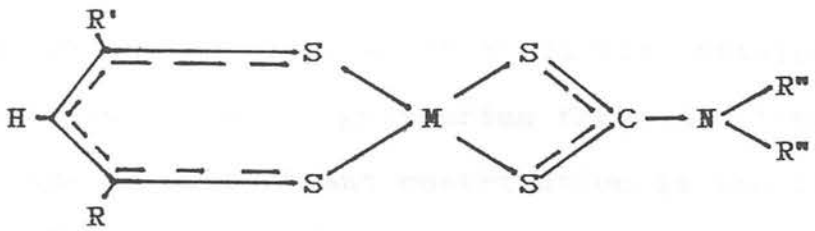
These two features have been previously witnessed in the parent complexes $[M(S_2C_3RHR')_2]$, with dominant ligand-character and little or no metal influence discovered in the LUMO.

These ordered behavioural patterns for the first-reduction processes $[M(S_2C_3RHR')_2]^{o/1-}$ and $[M(S_2C_3RHR')(S_2CNR"_2)]^{o/1-}$ (M=Ni, Pd, Pt) distinguish both from the metal-ion dependent reductions, $[M(S_2CNR"_2)_2]^{o/1-}$, which are rather scattered in comparison and appear at quite negative potentials. This

distinction is clearly represented in the data sets (a)-(c) and (d)-(f) of Table 4.2, with the accentuated potential differences between the platinum bis-dialkyldithiocarbamate complexes and the analogous $[Pt(S_2C_3RHR')(S_2CNR"_2)]$ systems particularly indicative of contrasting behaviour (i.e. a switch from metal-based to ligand-mediated redox-activity in the hybrid). The proposal of ligand-based hybrid reductions is strengthened when the $[M(S_2C_3CF_3HCH_3)(S_2CNR"_2)]$ systems, are considered. These complexes not only exhibit potentials which show little alteration throughout the triad, as previously discovered for $[M(S_2C_3CF_3HCH_3)_2]^{o/1-}$, but moreover, all $E^{o}red(1)$ values for these composite compounds are well-removed from the more negative M^{II}/M^{I} steps of $[M(S_2CNR"_2)_2]$, maintaining a near constant 300mV gap between $[M(S_2C_3CF_3HCH_3)_2]^{o/1-}$ and $[M(S_2C_3CF_3HCH_3)(S_2CNR"_2)]^{o/1-}$, regardless of the central metal ion.

Further evidence regarding the nature of the first hybrid reduction is gained from a systematic analysis of the substituent (R,R') influence on $E^{o}red(1)$, by means of a Reduction potential ($E^{o}red(1)$)/Substituent effect correlation. This correlation was tested using the hybrid series $[Ni(S_2C_3RHR')(S_2CN(i\text{-}C_3H_7)_2)]$ ((g)-(k), Table 4.2), where R,R'=CH_3,CH_3; CH_3,Ph; Ph,Ph; CF_3,CH_3 and CF_3,Ph. An electrochemical inductive parameter scale, derived by Heath and Leslie from similar correlation studies involving $[Pd(S_2C_3RHR')_2]$ systems[10], was employed in the

Table 4.2 Electrochemistry of Hybrid Complexes in 0.25M Bu_4NBF_4/CH_2Cl_2 vs. Ag/AgCl Reference



	M	R,R'	Bis-1,3-Parent $[M(S_2C_3RHR')_2]^{o/1-}$	Hybrid $[M(1,1\text{-}S_2)(1,3\text{-}S_2)]^{o/1-}$	Bis-1,1-Parent $[M(S_2CNR"_2)_2]^{o/1-}$	R"
(a)	Ni	CH_3, CH_3	-0.94V	-1.10V	-1.32V	C_2H_5
(b)	Pd	CH_3, CH_3	-0.96V	-1.12V	-1.48V	C_2H_5
(c)	Pt	CH_3, CH_3	-0.98V	-1.18V	-2.01V(†)	C_2H_5
(d)	Ni	CF_3, CH_3	-0.43V	-0.72V	-1.50V	$i\text{-}C_3H_7$
(e)	Pd	CF_3, CH_3	-0.38V	-0.65V	-1.48V	C_2H_5
(f)	Pt	CF_3, CH_3	-0.41V	-0.74V	-2.01V(†)	C_2H_5
(g)	Ni	CH_3, CH_3	-0.94V	-1.16V	-1.50V	$i\text{-}C_3H_7$
(h)	Ni	CH_3, Ph	-0.75V	-0.98V	-1.50V	$i\text{-}C_3H_7$
(i)	Ni	Ph, Ph	-0.61V	-0.85V	-1.50V	$i\text{-}C_3H_7$
(j)	Ni	CF_3, CH_3	-0.43V	-0.72V	-1.50V	$i\text{-}C_3H_7$
(k)	Ni	CF_3, Ph	-0.25V	-0.58V	-1.50V	$i\text{-}C_3H_7$
(l)	Ni	CH_3, CH_3	-0.94V	-1.10V	-1.33V	CH_3
(m)	Pt	CH_3, CH_3	-0.98V	-1.19V	-2.05V(†)	C_4H_9

(†) Electrochemical medium = 0.1M Bu_4NBF_4/CH_3CN

course of this study although the classical reported meta-Hammett[5] or classical Taft inductive parameters[1,8] would do equally well. Improved correlation coefficients for all $[M(S_2C_3RHR')_2]$ systems (M=Ni,Pd,Pt), obtained by the modified scale, largely arise from significant adjustment of the Ph-substituent contribution in the chelates.

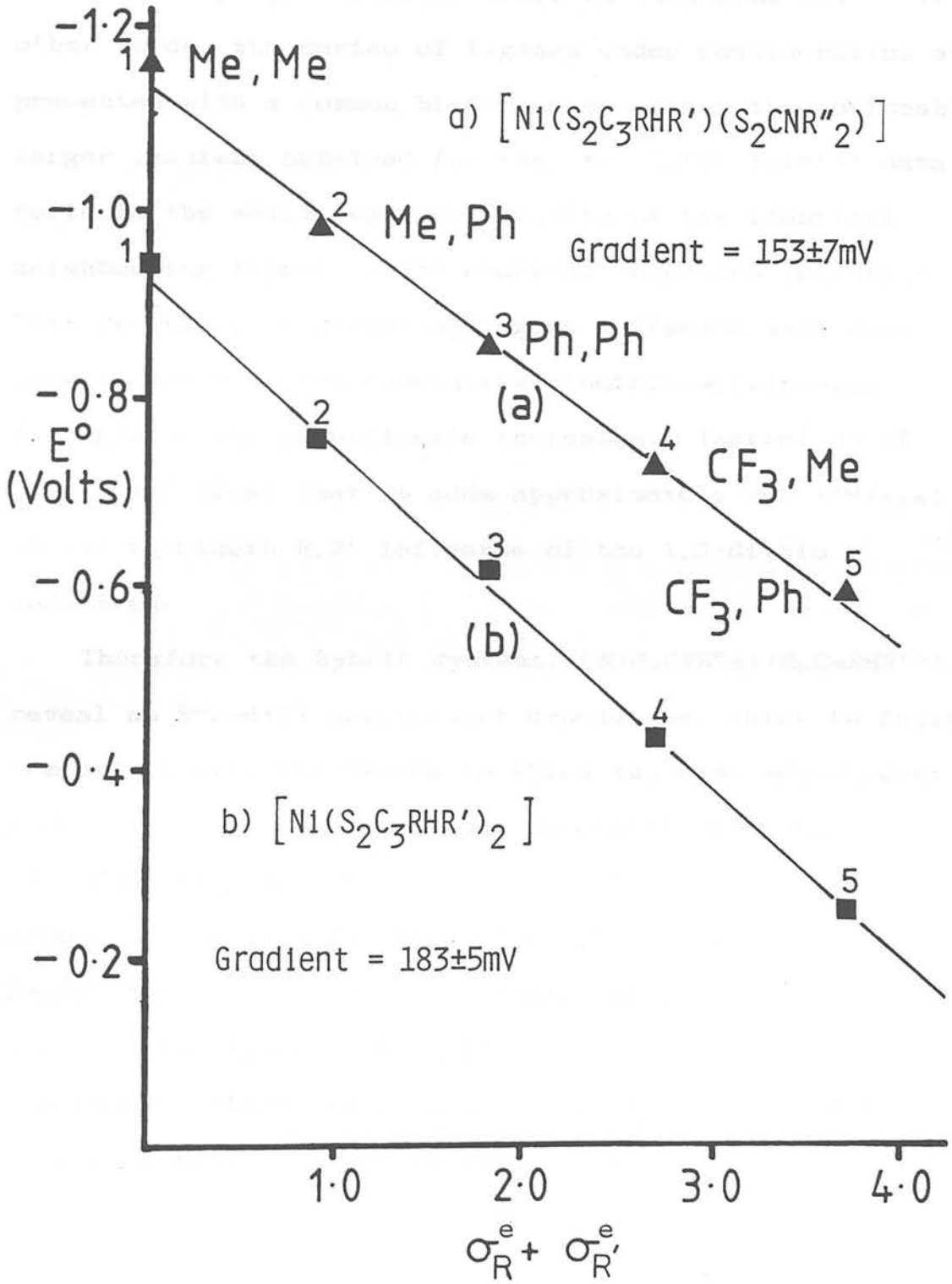
Therefore application of these same electrochemical inductive parameters to the analogous hybrids $[M(S_2C_3RHR')(S_2CNR"_2)]$ should provide a comparable linear correlation to that found in $[M(S_2C_3RHR')_2]$, if a similar redox-active orbital is involved. Normal Taft and electrochemically modified parameters are both shown in Table 4.3 below.

Table 4.3 Comparison of Substituent Inductive Parameters[10]

R	Taft (σ_R^*)	Electrochemical (σ_R°)
Bu^t	-0.30	-0.25
CH_3	0	0
Ph	+0.60	+0.90
CF_3	+2.70	+2.80

Figure 4.7 reveals a linear dependence of $E^{\circ}red(1)$ on the sum of the substituent inductive parameters, $\Sigma\sigma_R^{\circ}+\sigma_R^{\circ}$, for both the $[Ni(S_2C_3RHR')_2]^{0/1-}$ and $[Ni(S_2C_3RHR')(S_2CN(i-C_3H_7)_2)]^{0/1-}$ electron transfers. Least squares analysis produce gradients of 183±5 mV and 153±7 mV per unit for

Figure 4.7 - Substituent Sensitivity of Delocalised 1,3 - Dithio - Ring Nickel Complexes.



the respective metal - bis-1,3-dithio-β-diketonate and 1,1-dithio-1,3-dithio-hybrid correlations.

The smaller gradient observed for the hybrid $E^{o}red(1)$ versus $\Sigma\sigma_R^{o}+\sigma_R^{o}$ plot virtually establishes the true susbstituent influence for a single 1,3-dithio-β-diketonate ligand as the adjacent ligand is fixed (chosen to be di-isopropyldithiocarbamate in this data set). In other words, the series of ligands under consideration are presented with a common binding site. Thus the noticeably larger gradient obtained for the $[M(S_2C_3RHR')_2]^{o/1-}$ data reflects the additional contribution of the identical neighbouring ligand to the observed reduction potential. This secondary neighbouring-ligand influence must also grow linearly as the cumulative electron-withdrawing strength of the substituents increases. Inspection of Figure 4.7 shows that it adds approximately 20% ($^{30}/_{153}$) to the intrinsic R,R' influence of the 1,3-dithio reduction.

Therefore the hybrid systems, $[M(S_2CNR"_2)(S_2C_3RHR')]$, reveal an $E^{o}red(1)$ substituent dependence, which is fully compatible with the degree to which the same substituent groups influence the electrode potentials of both $[M(S_2C_3RHR')_2]$ and $[M(S_2C_2R_2)_2]$. This vindicates our preparative search for molecules containing an <u>isolated</u> SacSac-type ligand for electrochemical and spectroscopic studies, and appears to suggest that successive charge-trapped one-ligand reductions, coupled with secondary inductive effects, provide a workable model for the

reductive processes of the bis-1,3-dithio complexes, $[M(S_2C_3RHR')_2]$.

(b) Anodic Investigations

Initial oxidative scans (0 to +2.0V versus Ag/AgCl) of the hybrid systems reveal one strong irreversible wave, with the subsequent reverse scan displaying a much weaker wave, or two weaker waves near zero volts (as typified by $[M(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$, Figure 4.8). This oxidative behaviour looks remarkably similar to that found in the parent bis-1,3-dithio-β-diketonate complexes and suggests that the hybrid signals represent the oxidation of the (S_2C_3RHR') ligand to the dithiolium ion, followed by the reduction of this cation to the neutral radical (weaker signal observed in the reverse scan). The anodic electrochemical behaviour observed in the hybrids is summarised in Table 4.4.

Repetition of the hybrid oxidative cycle however results in the disappearance of both the signal assigned to the irreversible 2e ligand/dithiolium-ion oxidation and the subsequent dithiolium-ion reduction. This is a strong indication of electrode tarnishing taking place. This may explain the otherwise inconsistent features in the overall anodic behaviour of the hybrid complexes. In particular the observed voltammetric processes in the hybrid, whilst qualitatively resembling the anodic cycles of the parent $[M(S_2C_3RHR')_2]$ systems, do not exhibit a similar ordered

Figure 4.8 - Anodic Electrochemical Behaviour of $[Ni(S_2C_3CF_3HCH_3)(S_2CN(i\text{-}C_3H_7)_2)]$ in Dichloromethane.

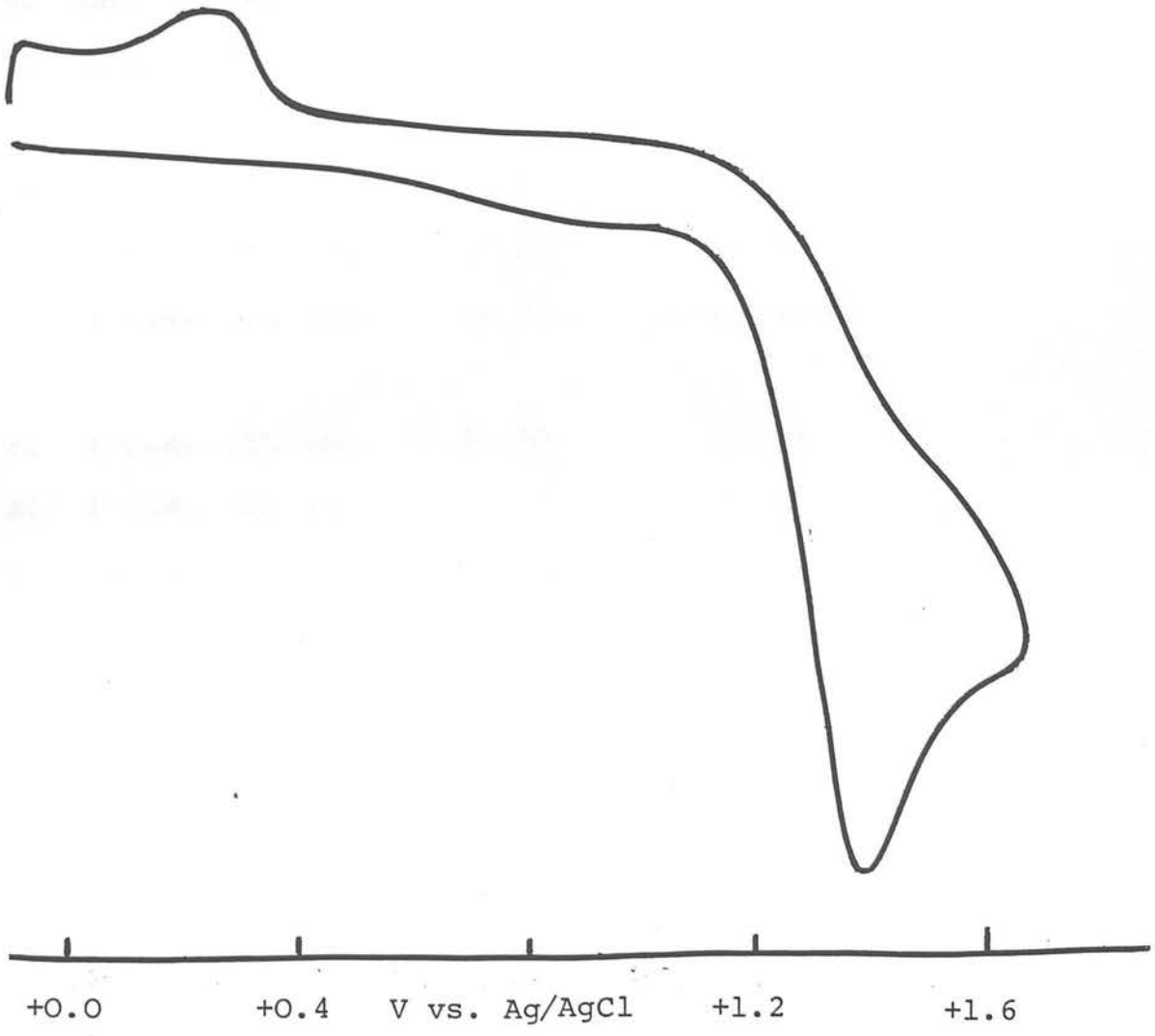


Table 4.4 Anodic Behaviour of $[M(S_2CNR''_2)(S_2C_3RHR')]$ Systems in 0.25M Bu_4NBF_4/CH_2Cl_2 vs. Ag/AgCl

Complex				Oxidation(V)	Subsequent Reduction(V)
M	R'	R	R'		
Ni	C_2H_5	CH_3	CH_3	+1.23	+0.25
Pd	C_2H_5	CH_3	CH_3	+1.54	-0.27
Pt	C_2H_5	CH_3	CH_3	+1.45	-0.17
Ni	CH_3	CH_3	CH_3	+1.14	+0.34
Pt	C_4H_9	CH_3	CH_3	+1.45	-0.16
Pd	C_2H_5	CF_3	CH_3	+1.80	(a)
Pt	C_2H_5	CF_3	CH_3	+1.64	-0.23
Ni	i-C_3H_7	CF_3	CH_3	+1.38	+0.20,+0.25
Ni	i-C_3H_7	CH_3	CH_3	+1.25	+0.16
Ni	i-C_3H_7	CH_3	Ph	+1.28	-0.13
Ni	i-C_3H_7	Ph	Ph	+1.24	-0.08

(a) Very broad and extremely weak signal, making an accurate assignment very difficult.

progression in potential, dependent upon the inductive influence of R and R' (irrespective of the metal centre), akin to known $[M(S_2C_3RHR')_2]$ oxidations and $[S_2C_3RHR']^+$ reductions[10] as shown in Table 4.5.

These gross discrepancies in E° values cannot be dismissed, and though we suspect they are artefacts of irreversible electrode surface phenomena, the assignment of the oxidative pathways adopted by the hybrid complexes should be regarded as an open question at this stage.

Table 4.5[10] Electrode Potentials for Electrochemically Derived 1,2-Dithiolium Ions[a] (vs. Ag/AgCl)

R,R'	$[M(S_2C_3RHR')_2] \xrightarrow{-4e} 2[S_2C_3RHR']^+ + M^{2+}$	$[S_2C_3RHR']^{o/+}$
Bu^t, Bu^t	+1.12V	-0.46V
CH_3, CH_3	+1.18V	-0.35V
Ph, CH_3	+1.23V	-0.09V
Ph, Ph	+1.37V	0.00V
CF_3, CH_3	+1.51V	+0.19V
CF_3, Ph	+1.69V	+0.30V

a) Potentials calculated at 85% of the forward peak current

4.3 Electrochemical Theory and Experimental

(a) Electrochemical Methods

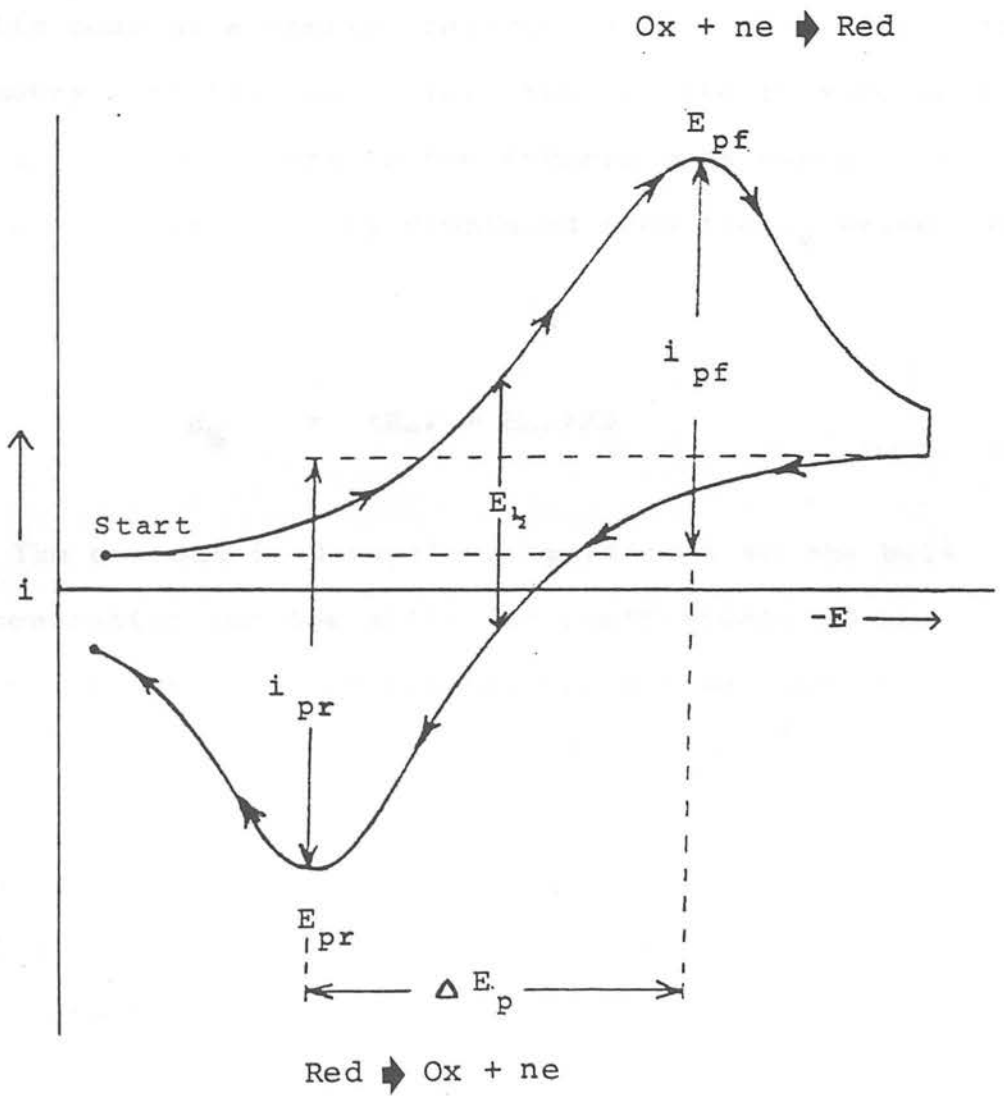
Cyclic voltammetric (C.V.) and a.c. voltammetric techniques were employed in the electrochemical studies of the hybrids $[M(S_2C_3RHR')(S_2CNR''_2)]$.

i) Cyclic Voltammetry

This method involves varying the potential of the stationary electrode linearly with time. The rate at which the potential is changed is recognised as the scan-rate, ν , and normally operates in the range 20-500mVs^{-1}. The scan-rate effectively controls the time-scale of the experiment.

Current responses in C.V. experiments are of peaked form, though asymmetric, with the forward (E_{pf}) and the reverse (E_{pr}) peak potentials well-defined and easily measured from the complete cyclic voltammetric trace (Figure 4.9). On scanning the potential of the electrode into the range where the reactant begins to be oxidised (or reduced) at the electrode, a current increase occurs and become more important as the potential gradually increases, due to an increase in the rate of the reaction occurring at the electrode surface. When the reaction has consumed most of the reactant near the electrode surface (in the absence of any stirring action), the current

Figure 4.9 - Summary of Classical Cyclic Voltammetric Parameters.



becomes limited by the rate at which additional reactant can diffuse to the electrode from the bulk of the solution. The current maximum occurs when the tendency towards increasing current is just matched by the trend towards decreasing current, imposed by the depletion of the reactant near the electrode surface. The latter of these two effects predominates beyond the peak, where the voltage scan direction is reversed in order to eventually cause the reversal of the forward electrode reaction, with a current maximum at E_{pf} (Figure 4.9).

The complete current wave form which results from the cyclic scan of a stable, reversible system is of a certain symmetry such that $i_{pf} = i_{pr}$, that is the forward peak current is equivalent to the reverse peak current, with the peaks symmetrically displaced from the $E_{½}$ value, such that

$$E_{½} = (E_{pf} + E_{pr})/2$$

The current is directly proportional to the bulk concentration and the diffusion coefficients of the electro-active species but the current maximum is also dependent upon scan rate, such that $i_p \propto \nu^{½}$. The bulk concentration undergoes negligible electrolysis in C.V. experiments, as the very small electrode surface area limits only μA currents to flow in the 10^{-3}M solutions under study.

ii) a.c. Voltammetry

Alternating current voltammetry (a.c.V.) essentially involves superimposing a small alternating potential upon the linear scanning (d.c.) potential and recording only the resultant alternating component of current as a function of the d.c. potential. The wave form assumes a peaked wave centred on the classical d.c. wave in the a.c. mode. The superimposed voltage is sinusoidal in form, with normally an amplitude of 10 mV, obtained in the frequency (ω) range 10-1000 Hz. The time-scale of the experiment is effectively controlled by the chosen frequency. Peak current is linearly dependent on $\omega^{\frac{1}{2}}$ and directly proportional to the bulk concentration.

A.c. voltammetry is an extremely useful electrochemical technique partly through its convenient peak wave and its ability to differentiate signals that are separated by as little as 40 mV (d.c. polarography requires a minimum separation of 200 mV to discriminate between two adjacent waves). A.c. voltammetry also is directly sensitive to the degree of reversibility, with signals suppressed by sluggish charge transfer.

iii) Reversibility Criteria

In order to establish whether a particular electrode process is both diffusion-limited and fully reversible (i.e. rapid electron-transfer in both forward and reverse

scanning directions), the system should conform to the classical electrochemical parameters listed in Table 4.6.

(b) Instrumentation

Voltammetric studies in 0.25 M Bu_4NBF_4/CH_2Cl_2 employed a PAR 170 Electrochemical system (potentiostat and programmer), interfaced with a Metrohm E505 cell stand and three electrode cell configuration. A non-aqueous $Ag/AgCl/Cl^-/CH_2Cl_2$ reference electrode (against which ferrocene was oxidised at +0.62V), separated by a further fritted salt-bridge and a platinum counter-electrode were used in a 5 ml or 10 ml jacketted glass cell. A.c. and cyclic voltammograms were obtained by use of a platinum wire or micro-disk working electrodes.

Cell solutions, normally $\approx 1.0 \times 10^{-3}$ molar in complex, were degassed with CH_2Cl_2-saturated argon and internal cell temperatures in the range 230-295 K were monitored using a Comark 5000 digital thermometer.

Routinely, all the electrochemistry was studied in CH_2Cl_2 due to the enhanced solubility of the parent complexes $[M(S_2C_3RHR')_2]$ in this medium. Acetonitrile however, was also employed in the study of the systems $[Pt(S_2CNR''_2)_2]$ ($R''=C_2H_5$, C_4H_9). This solvent involved the same basic set up as described above but 0.1 M Bu_4NBF_4 was found to be a sufficient electrolyte concentration. Acetonitrile was used as it affords a larger cathodic range than CH_2Cl_2, therefore enabling us to observe the

Table 4.6 Reversibility Criteria at 298K

A.C. Voltammetry	Cyclic Voltammetry
(a) $E_p = E_{1/2}$, independent of concentration.	(a) $\frac{1}{2}[E_{pf} + E_{pr}] = E_{1/2}$, independent of concentration and scan rate.
(b) Wave highly symmetric with a peak width 90 mV at half peak height.	(b) $i_{pf} = i_{pr}$, $\Delta Ep = 58$ mV
(c) i_p vs. $\omega^{1/2}$ plot is linear through the origin.	(c) i_{pf} vs. $\nu^{1/2}$ plot is linear through the origin.

extreme negative metal-based irreversible reductions of the two platinum bis-dialkyldithiocarbamates.

(c) Materials

All complexes described were prepared as detailed in Chapter 2. Electrochemical grade CH_2Cl_2 was stored over KOH pellets, then distilled from P_2O_5 immediately prior to use. Electrochemical grade acetonitrile was prepared by an initial four-stage purification[19] followed by distilling three times over P_2O_5. The Bu_4NBF_4 supporting electrolyte was prepared from Bu_4NOH and HBF_4, in water, recrystallised from a 1:1 ratio of analar methanol: water, then rigourously dried at 363K in vacuo.

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CHAPTER 5

Syntheses, Characterisation and Voltammetric Investigations of the Asymmetric [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$C$_3$CH$_3$HCH$_3$)] Complexes (M=Ni,Pd,Pt)

5.1 Introduction

Comprehensive voltammetric investigations of the delocalised systems $[M(S_2C_3RHR')_2]$ (M=Ni,Pd,Pt) by Heath and Leslie[1] have uncovered the orderly electrochemical character of the complexes $[Pd(S_2C_3RHR')_2]$, which enables the shift in $E^{\circ}red(1)$ between $[Pd(SacSac)_2]$ and any other $[Pd(S_2C_3RHR')_2]$ complex to be represented by equation (1),

$$\delta E(mV) = 100\ \Sigma\sigma^{*} = 200\ (\sigma^{*}_{R}+\sigma^{*}_{R\cdot}) \qquad (1)$$

where σ_R^* and $\sigma_{R\cdot}^*$ are electrochemically derived inductive parameters. The corresponding nickel and platinum systems exhibit near parallel relationships to those encountered in the seies of $[Pd(S_2C_3RHR')_2]$ complexes.

Unfortunately this wealth of data cannot determine whether the electron gained from the first reduction is 'trapped' on one ligand or delocalised over both chelate rings. As only symmetrical bis-complexes are available for examination (i.e. ligand a = ligand b), one obtains an equivalent correlation for both localised and delocalised models. In the localised approach; the electron is considered to be strongly influenced by the substituents on just one ligand:

$$\delta E(mV) = 200\ (\sigma^{*}_{R}+\sigma^{*}_{R\cdot})$$

exactly comparable to a delocalised model where, effectively, the electron spends half the time on each ligand:

$$\delta E(mV) = 200\ (\tfrac{1}{2}\sigma^{-}_{R}+\tfrac{1}{2}\sigma^{-}_{R\cdot}+\tfrac{1}{2}\sigma^{-}_{R}+\tfrac{1}{2}\sigma^{-}_{R\cdot})$$

$$\Rightarrow 200\ (\sigma^{-}_{R}+\sigma^{-}_{R\cdot})$$

However, the question of trapped or delocalised electron-acceptance and E^{o} substituent dependence in the reductions of $[M(S_2C_3RHR')_2]$ complexes can be pursued by investigating the electrochemical behaviour of metal - bis-1,3-dithio-β-diketonates with disimilar ligands complexed to the one metal centre ($R_1R_2 \neq R_3,R_4$). Hendrickson, Hope, and Martin have synthesised some complexes of this type (where $R_1, R_2 = OC_2H_5, CH_3$)[2] but their studies were restricted to the synthesis and routine characterisation of nickel(II) systems, and no electrochemical properties have thus far been reported for such asymmetric complexes.

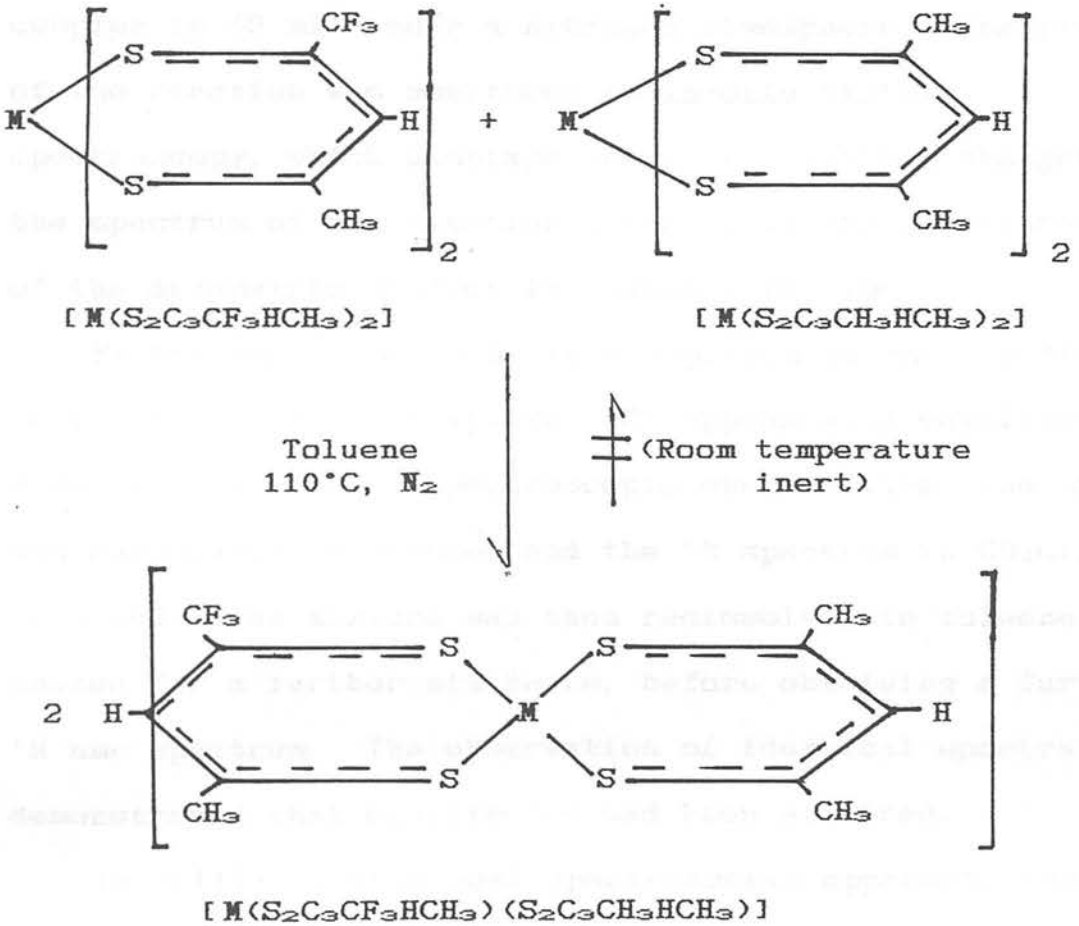
In order to investigate further the charge distribution of reduced $[M(S_2C_3RHR')_2]$ systems, we have synthesised new asymmetric complexes $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ (M=Ni,Pd,Pt). In this way we discovered, in conjunction with our electrochemical data for the hybrid reductions $[M(S_2C_3RHR')(S_2CNR''_2)]^{o/1-}$, that the two one-electron ligand-mediated reductions of $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ are, at least, consistent with <u>localised</u> electrochemical behaviour. Essentially we have managed to show that the 1st E^{o} value is precisely <u>characteristic</u> of a <u>localised</u>

reduction of the more electron-withdrawing ligand ($S_2C_3CF_3HCH_3$), and equally that the second reduction is precisely <u>characteristic</u> of a <u>localised</u> reduction of the less electron withdrawing ligand ($S_2C_3CH_3HCH_3$).

5.2 Synthesis of [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$C$_3$CH$_3$HCH$_3$)] Systems

Scheme 5.1 below shows the preparative route to these complexes:

Scheme 5.1



The T_{∞} solution is a statistical 1:2:1 mixture for the Pd and Pt systems (although approximately 1:4:1 for Ni), rather than exhaustive conversion to the mixed species. Thus chromatographic separation is essential for the isolation of the asymmetric mixed product. The success of this separation of the scrambled product from the reactants

is dependent upon the reaction being irreversible at room temperature, i.e. the synthesised mixed product is stable towards disproportionation.

Preparation of the reactants was carried out as described in Section 2.2. The mixed complexes were then obtained by boiling equimolar amounts of the appropriate starting materials in toluene (e.g. 0.1 mmole of each complex in 45 ml) under a nitrogen atmosphere. The progress of the reaction was monitored by in-situ visible spectroscopy, which displays small but distinct changes in the spectrum of the reaction mixture, as the concentration of the asymmetric product increases with time.

Proton nmr comparisons were employed to confirm that the reaction was really complete. On approaching equilibrium according to visible spectroscopic observations, the mixture was evaporated to dryness and the ^1H spectrum in CD_2Cl_2 obtained. The mixture was then redissolved in toluene and heated for a further six hours, before obtaining a further ^1H nmr spectrum. The observation of identical spectra demonstrated that equilibrium had been attained.

In utilizing this dual spectroscopic approach, the reaction rate to attain equilibrium was found to be similar for all three hybrids (12 hours at 0.1 mmolar for Ni,Pd; 20 hours at 0.05 mmolar for Pt). Attempts to monitor the progress of the reactions by in-situ ^1H nmr studies in d^8-toluene were not pursued, as the strong residual solvent resonances in the methyl region of the spectrum (2-1.5 ppm) obscurred the methyl signals of all three dithio-systems.

Other nmr solvents were found to be unsuitable on the grounds of reactant insolubility, or low boiling point (too low to support the scrambling reaction).

Proton nmr investigations have shown that the final equilibrium mixture consists of a 1:2:1 statistical distribution of $[M(S_2C_3CF_3HCH_3)_2]$: $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$: $[M(S_2C_3CH_3HCH_3)_2]$ for the Pd and Pt systems, with 1:4:1 more favourable for the Ni reaction. These product distributions from the reactions involving two π-acceptor ligands are notably different to the exhaustive scrambling previously found in the hybrids $[M(S_2CNR''_2)(S_2C_3RHR')]$. This observation emphasises the mutually beneficial effect of combining π-donor and π-acceptor ligands, which we suggest is responsible for the exclusive or very high yields of the 1,1-dithio-1,3-dithio hybrid product.

The separation of each mixed complex from the reactants was carried out by initially testing the suitability of single and mixed solvent eluents (in varying proportions) on small-scale silica-coated thin-layer chromatographic plates. Having established the best eluent for each of the three reaction mixtures, based on many trials, isolation of the mixed product $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ was perfectly feasible at room temperature without reversion to the reactants. This involved the use of a silica-packed chromatographic column (M=Pd) or commercial high performance silica-coated preparative-scale thin-layer chromatographic plates (M=Ni,Pt). Characterisation of the purified product

was established by mass spectroscopy, ^{1}H nmr and electronic spectroscopy, prior to electrochemical investigations. As only small amounts of each isolated composite complex were obtained (5 - 20 mg), no re-crystallisations were attempted.

Infra-red spectroscopy (4000-250 cm^{-1}), using KBr disks, shows the spectra of the mixed products to consist of almost exact superpositions of the parent spectra, with no new vibrational bands. Likewise, the absorption bands found in the electronic spectra of the mixed products closely suggest a superposition of the bands observed in the two parent bis-complexes, $[M(S_2C_3CF_3HCH_3)_2]$ and $[M(S_2C_3CH_3HCH_3)_2]$. Proton nmr studies are likewise essentially additive but once again confirm the small but important mutual influence of the neighbouring ligands. Mass spectroscopic investigations reveal three major m/e signals in every case, corresponding to the parent ion and the two dithiolium ions, $(S_2C_3CF_3HCH_3)^+$ and $(S_2C_3CH_3HCH_3)^+$, derived from the two 1,3-dithio-β-diketonate ligands.

The particular experimental procedures employed to obtain each specific complex are reported below.

[(dithio-acetylacetonato)(dithio-1,1,1-trifluoroacetylacetylacetonato) nickel(II)]

$[Ni(S_2C_3CH_3HCH_3)(S_2C_3CF_3HCH_3)]$ $NiC_{10}H_{11}S_4F_3$

$[Ni(S_2C_3CF_3HCH_3)_2]$ (0.043g, 0.1mmole) and $[Ni(S_2C_3CH_3HCH_3)_2]$ (0.033g, 0.1mmole) were dissolved in nitrogen-flushed toluene (45ml). The resulting solution was

slowly stirred and the passage of N_2 maintained whilst the system was heated to 110°C for a period of eighteen hours ('H nmr studies showed that the reaction was complete after twelve hours had elapsed). After removing, by filtration, some insoluble solid produced by decompositions, the solvent was evaporated to yield 0.054g of a wine-coloured solid. The hybrid product was subsequently isolated from the two precursors using silica-coated preparative thin-layer chromatographic plates and a mixed eluent of CCl_4:CH_2Cl_2 (3:1). An oily product was converted to a wine-coloured solid by the addition of ether.

Yield = 0.009g (12%, or 18% of maximum based on 1:4:1 equilibrium ratio)

Mass Spectrum: m/e 374$[^{58}Ni(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^+$

m/e 185$[(S_2C_3CF_3HCH_3)]^+$

m/e 131$[(S_2C_3CH_3HCH_3)]^+$

[(dithio-acetylacetonato)(dithio-1,1,1-trifluoroacetylacetonato) palladium(II)]

$[Pd(S_2C_3CH_3HCH_3)(S_2C_3CF_3HCH_3)]$ $PdC_{10}H_{11}S_4F_3$

$[Pd(S_2C_3CF_3HCH_3)_2]$ (0.05g, 0.1mmole) and $[PdS_2C_3CH_3HCH_3)_2]$ (0.039g, 0.1mmole) were dissolved in nitrogen-flushed toluene (45ml). The resulting solution was slowly stirred and the passage of N_2 maintained whilst the system was heated to 110°C for a period of fifteen hours ('H

nmr showed reaction to be complete after twelve hours had elapsed). No decomposition was observed. The solvent was removed to yield 0.085g of a violet solid.

Separation of the various components was then carried out using a silica packed chromatographic column. 60/80 petroleum ether was initially employed to isolate $[Pd(S_2C_3CF_3HCH_3)_2]$ from its rather more insoluble counterparts. A final mixed eluent of 60/80 petroleum ether: chloroform (4:1) was then used to separate the hybrid product from $[Pd(S_2C_3CH_3HCH_3)_2]$. The hybrid was originally obtained as an oil, but yielded a purple solid in contact with ether.

Yield = 0.018g (20% or 40% of maximum based on 1:2:1 equilibrium ratio).

Mass Spectrum: m/e 422$[^{106}Pd(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^+$

m/e 185$[(S_2C_3CF_3HCH_3)]^+$

m/e 131$[(S_2C_3CH_3HCH_3)]^+$

[(dithio-acetylacetonato)(dithio-1,1,1-trifluoroacetylacetonato) platinum(II)]

$[Pt(S_2C_3CH_3HCH_3)(S_2C_3CF_3HCH_3)]$ $PtC_{10}H_{11}S_4F_3$

$[Pt(S_2C_3CF_3HCH_3)_2]$ (0.028g, 0.05mmole) and $[Pt(S_2C_3CH_3HCH_3)_2]$ (0.023g, 0.05mmole) were dissolved in nitrogen-flushed toluene (40ml). The resulting solution was slowly stirred and the passage of N_2 maintained whilst the

system was heated to 110°C. ^{1}H nmr spectroscopy revealed that the reaction was complete after a period of twenty hours.

The system was then immediately filtered and the solvent removed to produce 0.036g of solid. Separation of the three components was then completed using silica-coated preparative thin-layer chromatographic plates and a mixed eluent of CCl_4:CH_2Cl_2 (3:1). An oily product was converted to a blue/purple solid on contact with ether.

Yield = 0.006g (12% or 24% of maximum based on 1:2:1 equilibrium ratio).

Mass Spectrum: m/e 511[$Pt(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)$]$^+$

The dithiolium ion traces are present in the spectrum but are of weaker intensity (particularly the m/e signal for $(S_2C_3CF_3HCH_3)^+$) than those signals found in the Ni and Pd centred mixed systems.

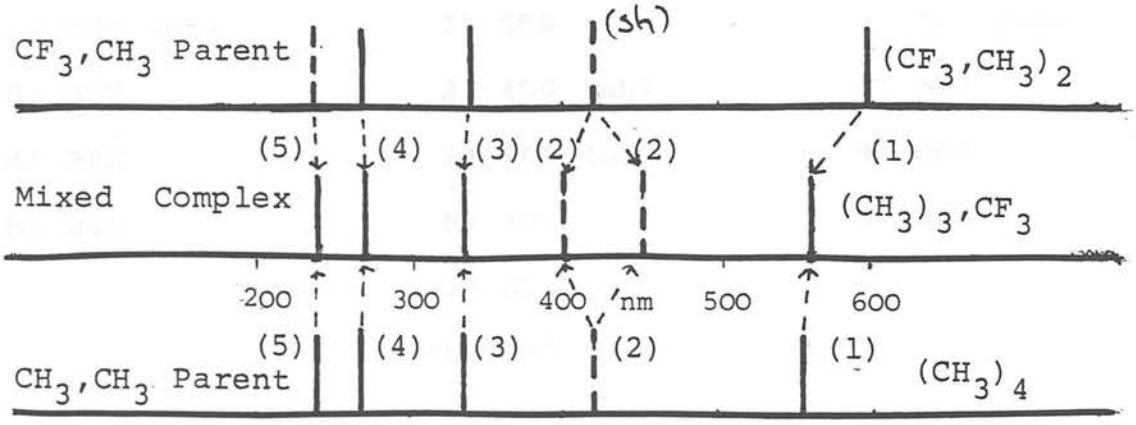
5.3 Spectroscopic Characterisation

a) Electronic Spectroscopy

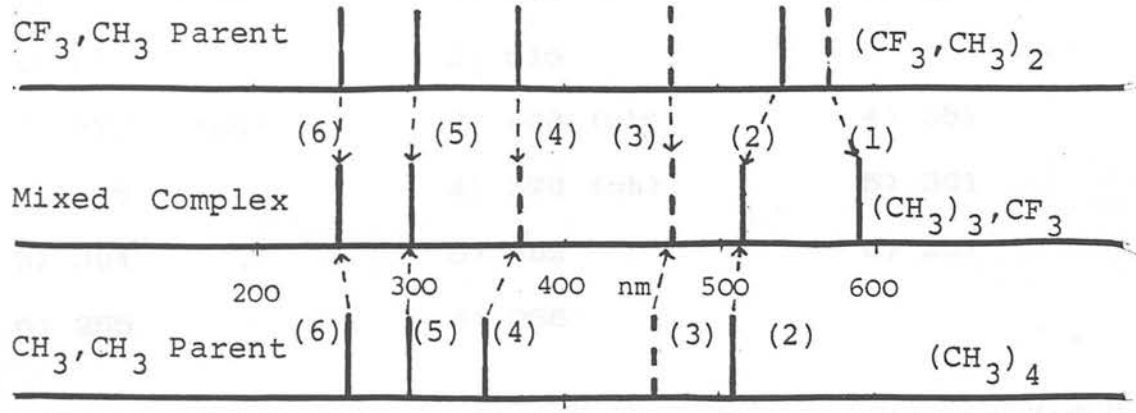
Similar band sequences emerge from the spectra of all three hybrids [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)] (M=Ni,Pd,Pt), as the absorption bands discovered in these mixed compounds can in almost every case be directly associated with the bands found in the two parent complexes [M($S_2C_3CF_3HCH_3$)$_2$] and [M($S_2C_3CH_3HCH_3$)$_2$]. Figure 5.1 clearly demonstrates this simple additive effect. Moreover, these approximate superpositions (i.e. hybrid spectrum = parent spectrum(1) + parent spectrum(2)) suggest that the two ligand chromophores are largely independent and non-interacting. A comparison of hybrid and parent spectra is presented in Table 5.1.

Figure 5.1 - Schematic Comparison of $[M(S_2C_3RHCH_3)_2]$ (R=CF_3,CH_3) and $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ Electronic Spectra.

Nickel Systems



Palladium Systems



Platinum Systems

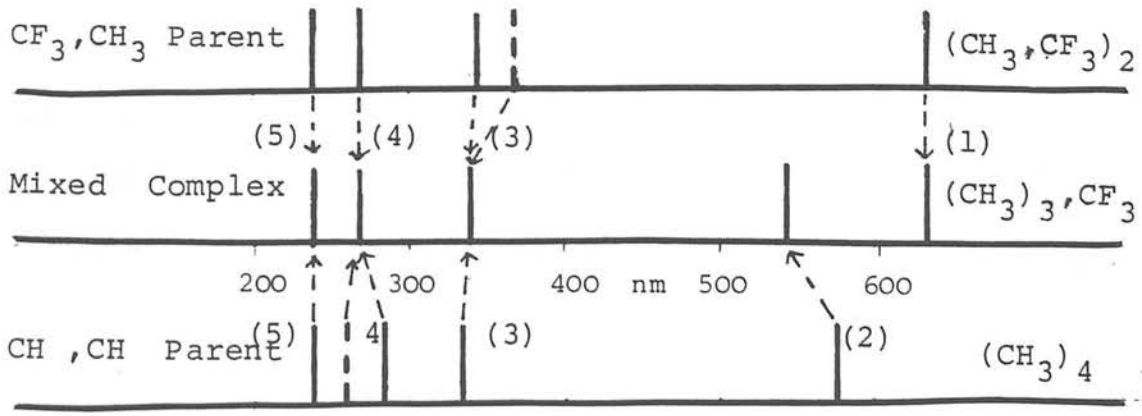


Table 5.1 Electronic Spectra of

[M($S_2C_2CF_3HCH_3$)($S_2C_2CH_3HCH_3$)]

[Ni($S_2C_2CF_3HCH_3$)$_2$]	[Ni($S_2C_2CF_3HCH_3$)($S_2C_2CH_3HCH_3$)]	[Ni($S_2C_2CH_3HCH_3$)$_2$]
1) 594 nm	740 nm	1) 556 nm
2) 420 (sh)	1) 559	2) 420 (sh)
3) 337	2) 450 (sh)	3) 336
4) 272	2) 400 (sh)	4) 268
5) 242	3) 335	5) 242
	4) 270	
	5) 242	

[Pd($S_2C_2CF_3HCH_3$)$_2$]	[Pd($S_2C_2CF_3HCH_3$)($S_2C_2CH_3HCH_3$)]	[Pd($S_2C_2CH_3HCH_3$)$_2$]
1) 570 nm(sh)	1) 592 nm	2) 509 nm
2) 543	2) 515	3) 460 (sh)
3) 472 (sh)	3) 468 (sh)	4) 352
4) 368	4) 370 (sh)	5) 301
5) 304	5) 302	6) 257
6) 255	6) 256	

[Pt($S_2C_2CF_3HCH_3$)$_2$]	[Pt($S_2C_2CF_3HCH_3$)($S_2C_2CH_3HCH_3$)]	[Pt($S_2C_2CH_3HCH_3$)$_2$]
1) 635 nm	1) 636 nm	2) 574 nm
370 (sh)	2) 545	3) 336
3) 344	3) 342	4) 286
4) 268	4) 272	4) 263 (sh)
5) 240	5) 237	5) 242

Table 5.1 (Cont'd)

Notes

(a) Accurate extinction coefficients were not obtained for the hybrid complexes, due to the limitation of no recrystallised material.

(b) Numerical identification of the bands refers to relationships depicted in Figure 5.1.

(c) (sh) refers to a shoulder.

(d) Spectra were obtained on a Pye-Unicam SP4-800 Spectrometer, in the range 200-800 nm, in CH_2Cl_2.

(b) 'H Nmr Spectroscopy

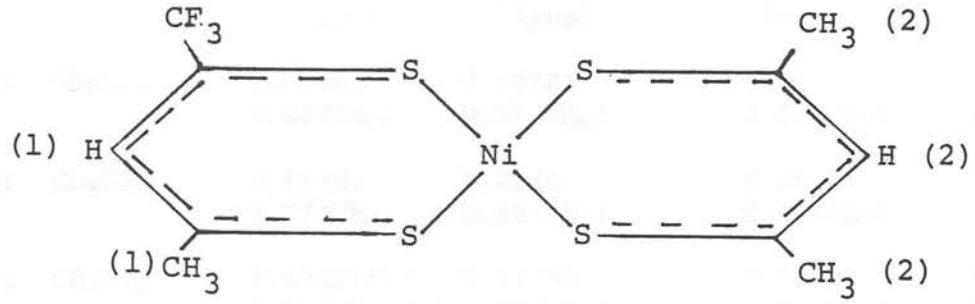
The 'H nmr spectra of the diamagnetic asymmetric complexes [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)], M=Ni,Pd,Pt, (typified by [Ni($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)], displayed in Figure 5.2) reveal chemical shift values which slightly differ from those found in the parent complexes [M($S_2C_3CF_3HCH_3$)$_2$] and [M($S_2C_3CH_3HCH_3$)$_2$] (Table 5.2 and Figure 5.3). This observation once again demonstrates the small shift contributions made by the neighbouring ligand. In considering the methine proton chemical shifts, the magnitude of the remote substituent influence is approximately +0.06 (±0.02) ppm for CF_3 in ($S_2C_3CF_3HCH_3$), identical to that deduced in Section 2.6(b). In fact, the neighbouring ligand influence on the methine proton increases in the order Pd<Ni≈Pt, as displayed in Figure 5.3.

Further inspection of Figure 5.3 shows that the methyl resonances for the Pt complexes shift to substantially lower frequencies relative to the Pd and Ni analogues, and that the internal shifts between the parent and the mixed system are also amplified in the order Pd<Ni<<Pt.

This sequence parallels the similar trends previously noted in [M(SacSac)$_n$]^{3,4} (M=Ni^{II}, Pd^{II}, Pt^{II}; Co^{III}, Rh^{III}, Ir^{III}), [M($SOC_3(OC_2H_5)HCH_3$)] (M=Ni^{II}, Pd^{II}, Pt^{II}; Co^{III}, Rh^{III}, Ir^{III}) [5,6] and [M(S_2C_3RHR')($S_2CNR''_2$)], in Chapter 2. Table 5.3 summarises the chemical shift displacements observed in the parent/mixed complex transition.

Figure 5.2 - ^{1}H Nmr Spectrum of

[Ni($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)]



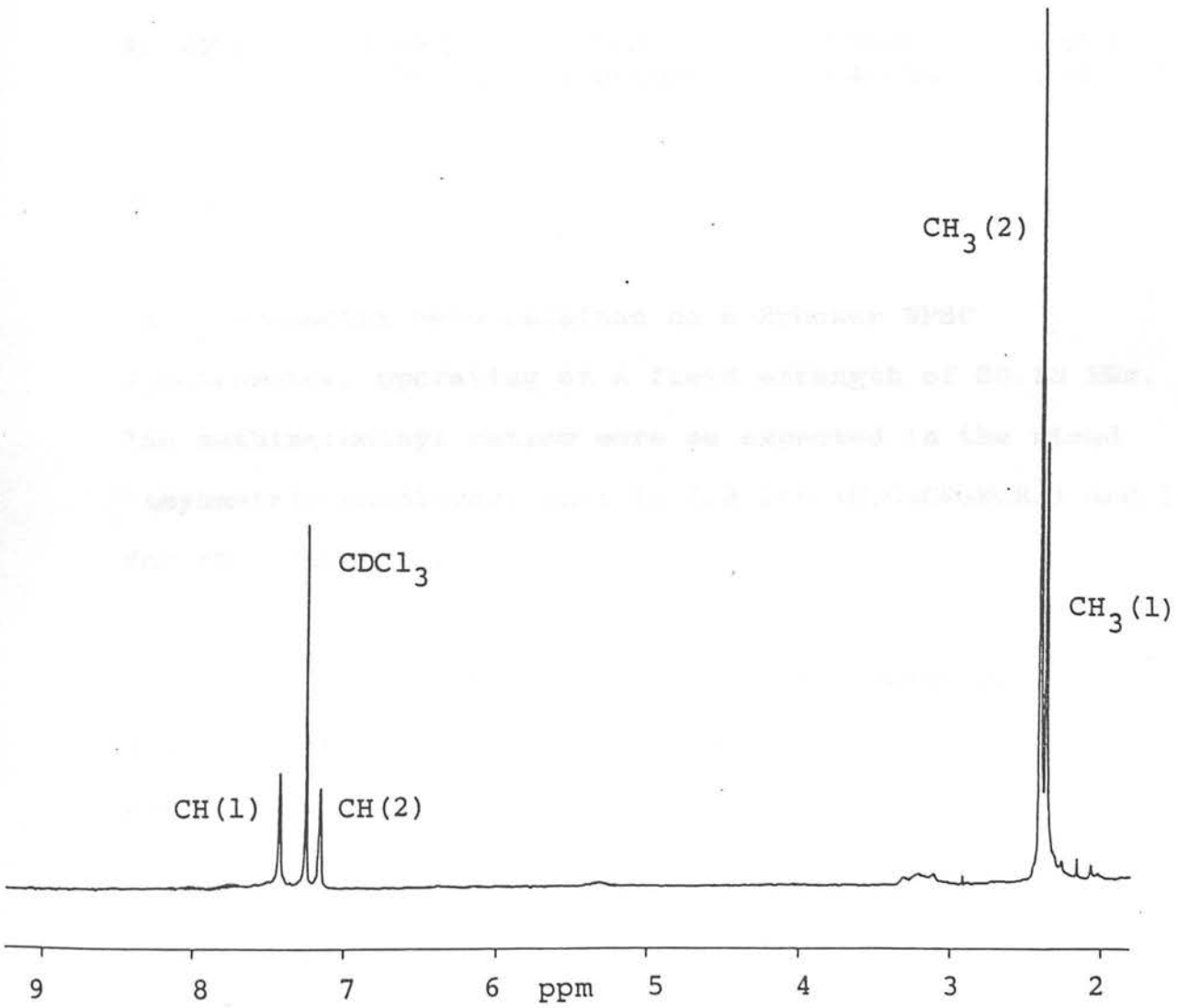


Table 5.2 - [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)] Proton Nmr Data[a]

		Mixed Complex		Parent Complexes	
M	Solvent	($S_2C_3CF_3HCH_3$) (ppm)	($S_2C_3CH_3HCH_3$) (ppm)	($S_2C_3CF_3HCH_3$) (ppm)	($S_2C_3CH_3HCH_3$) (ppm)
Pd	CD_2Cl_2	7.55(H) 2.60(CH_3)	7.25(H) 2.57(CH_3)	7.60(H) 2.67(CH_3)	7.20(H) 2.51(CH_3)
Ni	CD_2Cl_2	7.47(H) 2.37(CH_3)	7.22(H) 2.42(CH_3)	7.56(H) 2.47(CH_3)	7.15(H) 2.35(CH_3)
Pt	CD_2Cl_2	7.42(H)[c] 2.06(CH_3)[b]	7.17(H) 2.25(CH_3)	7.50(H) 2.22(CH_3)	7.10(H) 2.13(CH_3)
Pd	$CDCl_3$	7.49(H) 2.57(CH_3)	7.18(H) 2.54(CH_3)	7.53(H) 2.63(CH_3)	7.14(H) 2.49(CH_3)
Ni	$CDCl_3$	7.43(H) 2.36(CH_3)	7.16(H) 2.40(CH_3)	7.50(H) 2.45(CH_3)	7.10(H) 2.34(CH_3)

Notes

(a) The spectra were obtained on a Brücker WP80 spectrometer, operating at a field strength of 80.13 MHz. The methine:methyl ratios were as expected in the mixed asymmetric complexes, that is 1:3 for ($S_2C_3CF_3HCH_3$) and 1:6 for ($S_2C_3CH_3HCH_3$).

(b) The methyl signals in the platinum complex exist as 1:4:1 triplets, with the platinum satellites found at the positions shown below:

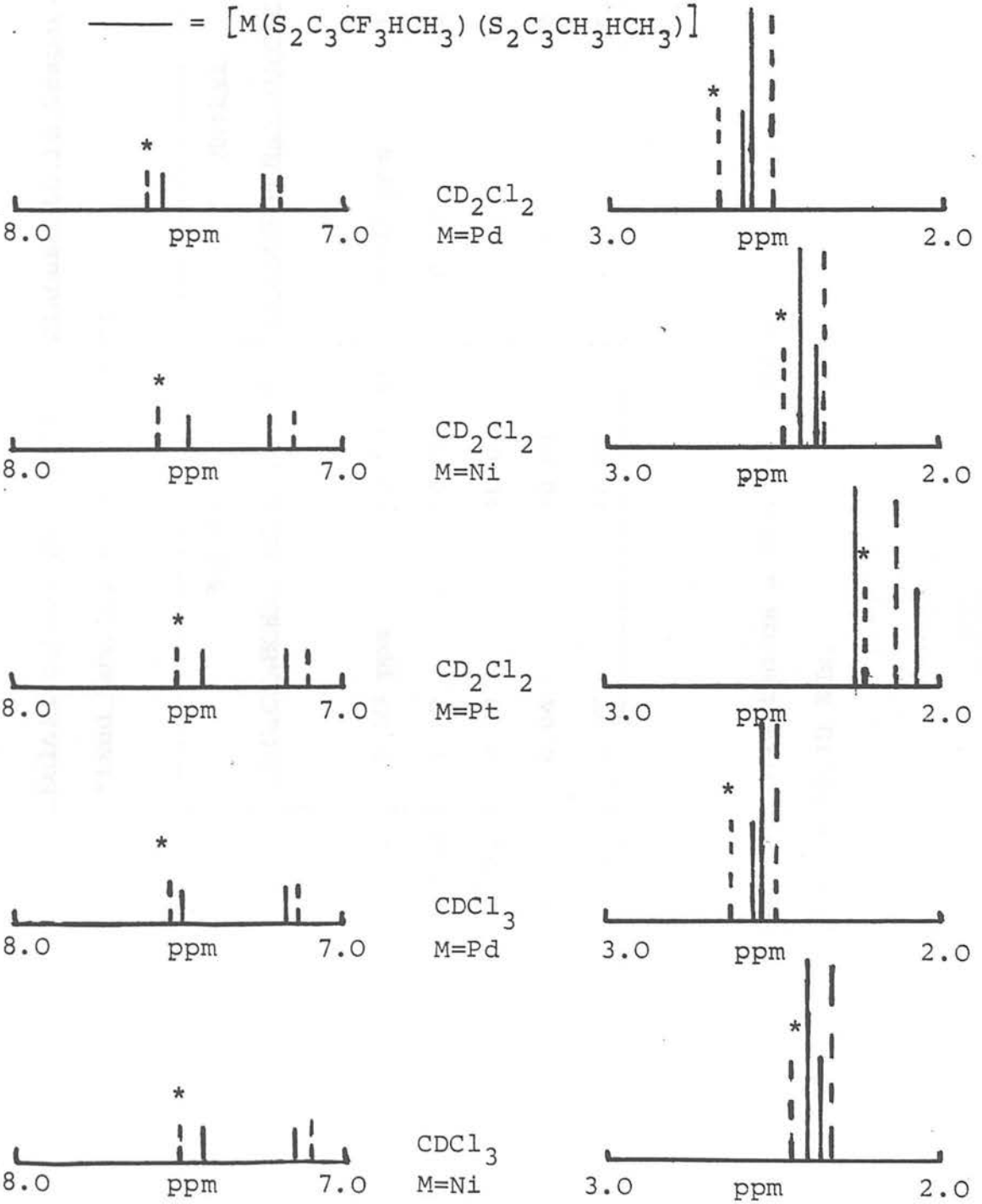
Complex	Satellites (ppm)	$^4J(Pt-CH_3)$ (Hz)
$[Pt(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$	2.11, 2.02 2.30, 2.19	7.1 8.8
$[Pt(S_2C_3CF_3HCH_3)_2]$	2.27, 2.17	7.7
$[Pt(S_2C_3CH_3HCH_3)_2]$	2.18, 2.08	8.4

(c) Satellites from the $^4J_{Pt-H}$ couplings were undetected.

Figure 5.3 - Schematic Representation of $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ and $[M(S_2C_3RHCH_3)_2]$ (R=CF_3,CH_3) Chemical Shifts.

* - - - = $[M(S_2C_3CF_3HCH_3)_2]$; - - - = $[M(S_2C_3CH_3HCH_3)_2]$

——— = $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$



Methine Proton

Methyl Protons

Table 5.3 Relative Chemical Shift Displacements in Comparing Mixed Complex with Parents[a]

M	Solvent	Methine ($S_2C_2CF_3HCH_3$)	Methine ($S_2C_2CH_3HCH_3$)	Methyl ($S_2C_2CF_3HCH_3$)	Methyl ($S_2C_2CH_3HCH_3$)
Pd	CD_2Cl_2	−0.05 ppm	+0.05 ppm	−0.07 ppm	+0.06 ppm
Ni	CD_2Cl_2	−0.09	+0.07	−0.10	+0.07
Pt	CD_2Cl_2	−0.08	+0.07	−0.16	+0.12
Pd	$CDCl_3$	−0.04	+0.04	−0.06	+0.05
Ni	$CDCl_3$	−0.07	+0.06	−0.09	+0.06

(a) Spectra collected on a Brücker WP80 Spectrometer, operating at a strength of 80.13 MHz.

5.4 Electrochemical Studies of [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$C$_3$CH$_3$HCH$_3$)] Asymmetric Mixed Complexes (M=Ni,Pd,Pt)

Identical electrochemical pathways are pursued by all three [M(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$C$_3$CH$_3$HCH$_3$)] systems in both the reductive and oxidative scans, with a possible dimerisation of the first reduced species evident in all three mixed complexes. Cyclic and a.c. voltammetric investigations of all three systems in a 0.5M Bu_4NBF_4/CH_2Cl_2 medium (using identical instrumentation to that outlined in Section 4.3(b)) readily identify the existence of similar reductive pathways in each hybrid complex, typified by the voltammograms of [Pd(S$_2$C$_3$CF$_3$HCH$_3$)(S$_2$C$_3$CH$_3$HCH$_3$)] in Figure 5.4. Scheme 5.2 summaries the electrode processes that are observed.

Scheme 5.2

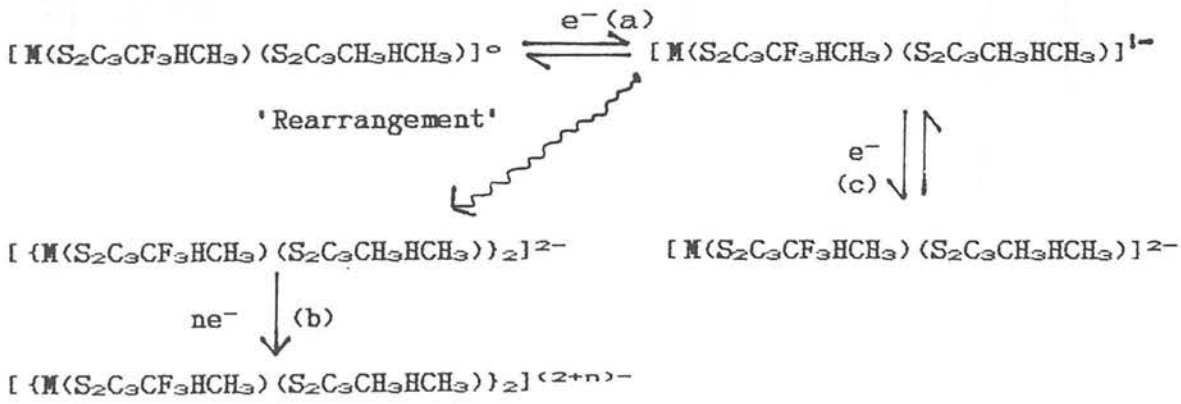
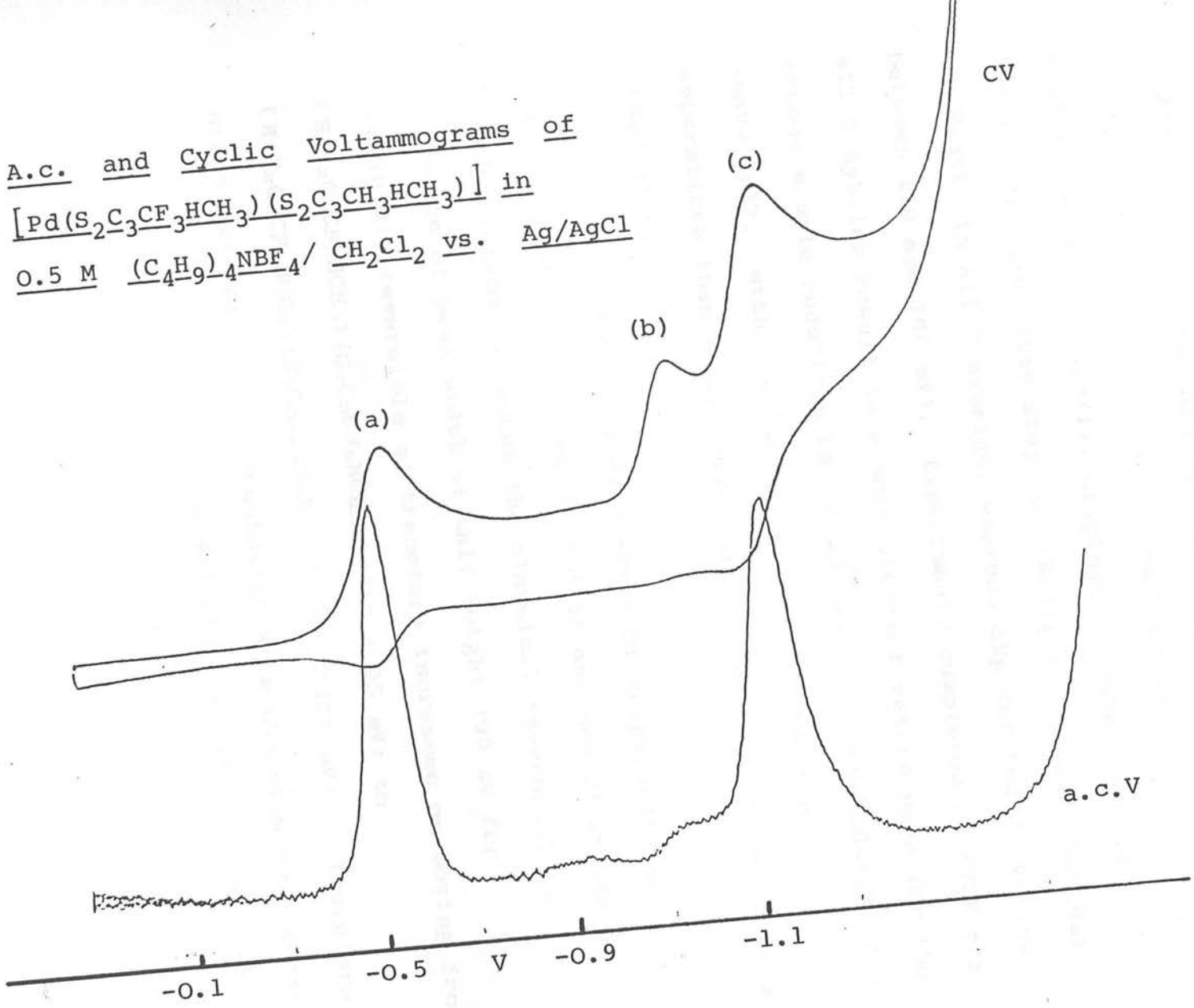


Figure 5.4 - A.c. and Cyclic Voltammograms of $[Pd(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ in 0.5 M $(C_4H_9)_4NBF_4$/ CH_2Cl_2 vs. Ag/AgCl



Step (b) proceeds at lower potentials than step (c) in all three hybrid complexes.

Although steps (a) and (c) both represent two one-electron reductions (i.e. Red(1) and Red(2) of the intact complex), step (a) (Red(1)) displays a faster rate of electron transfer than step (c) (Red(2)). (Thus, $\Delta Ep \simeq 60mV$ for Red(1) in all 3 hybrids, whereas ΔEp for Red(2) varies between 110 and 160 mV). Experiments completed at 223K for all 3 hybrids result in a more distinct return wave for the second simple reduction $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{1-/2-}$ (wave (c)), with smaller forward to reverse peak separations than those found for the same reduction at room temperature.

A.c. voltammetry reveals waves of comparable intensity for the processes located at Red(1) and Red(2) in the Pd and Pt systems, although the classical reversibility criterion of peak width at half height (90 mV for completely reversible e^- transfer) increases on moving from $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ (~95 mV) to $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{1-/2-}$ (~120 mV). Therefore steps (a) and (c) are consistent with stepwise one-electron reductions of the two adjacent chelate rings. Step (a) exhibits near classical electrochemical reversibility criteria, whereas step (c) is only quasi-reversible.

Although the species represented by wave (b) cannot be established at this stage, a dimer of the first reduced species may be a plausible assignment, analogous to that found through kinetic studies in the parent systems[1].

$$[M(SacSac)_2]^{1-} \xrightarrow{k_m} [\{M(SacSac)_2\}_2]^{2-};\ k_{Pt} > k_{Pd} >> k_{Ni}$$

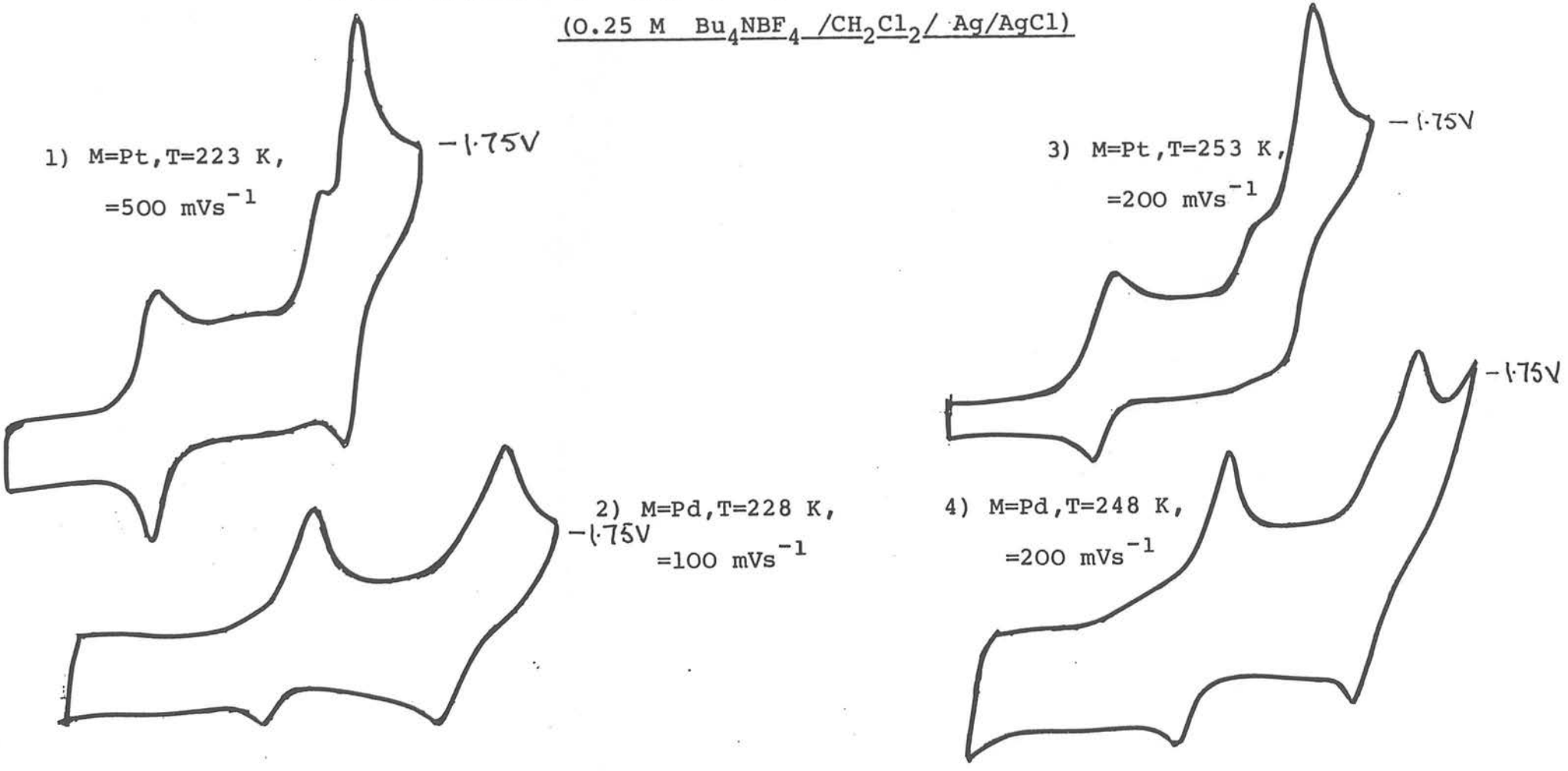
Dimers of metal-bis-1,2-dithiolate complexes have also been widely reported[7-9], with X-ray crystallographic studies determining that dimeric systems, involving 1,2-dithiolate ligands, are also found in nickel group chemistry e.g. the mixed system $[Ni(S_2C_2(CF_3)_2)(S_2CN(C_2H_5)_2)]_2$ [10] and the palladium and platinum centred complexes, $[M(S_2C_4H_4)_2]_2$ [11]. Moreover, weak interactions have also been previously detected between monomeric dithiolene anions[12-14].

Cyclic voltammetric investigations of all 3 hybrids at low temperatures and fast scan rates once again reveal that this rearrangement occurs quickest for the platinum complex, as in the parent complexes $[M(SacSac)_2]$, with wave (b) least prominent in the Ni hybrid. The effective rate of rearrangement (Pt>Pd>Ni) is best demonstrated by noting that wave (b), which represents the rearranged species is still evident on scanning at 500 mVs^{-1} at 223K in the Pt-centred complex, whereas scan rates of 10 Vs^{-1} at 290K (or 100 mVs^{-1} at 223K) for the Pd hybrid and 500 mVs^{-1} at 290K for the nickel hybrid, both result in the virtual disappearance of step (b). Figure 5.5 contrasts the effect of varying temperature and scan-rate on the cyclic voltammograms of the Pd and Pt systems.

Almost identical current responses in stirred cyclic voltammograms suggest that processes (a) and (c) both involve one electron. There is a notable similarity in the

Figure 5.5 - Cyclic Voltammetric Temperature and Scan-rate Dependence in $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ Systems (M=Pd,Pt)

(0.25 M Bu_4NBF_4 /CH_2Cl_2/ Ag/AgCl)



reduction potentials for step (b) in all three hybrids [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)]; -1.30V(Ni), -1.21V(Pd) and -1.28V(Pt). These parallel reduction potentials of the reputed dimer suggest a ligand-mediated process is responsible for the emergence of wave (b).

Therefore initial voltammetric evidence implies that the first reduced species of the hybrids, [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)]$^{1-}$, participate in dimerisation processes which are less effective than those observed in the parent systems [M(SacSac)$_2$]. The dimerisation of the mixed product is probably not as prominent due to the steric bulk of the CF_3 substituents which suppress the possible dimerisation of [M($S_2C_3CF_3HCH_3$)$_2$]$^{1-}$. A summary of the two ligand reductions and the rearrangement step of all three hybrid complexes are presented in Table 5.4, in association with the E°red(1) and E°red(2) values of the parent compounds [M(SacSac)$_2$] and [M($S_2C_3CF_3HCH_3$)$_2$].

Two irreversible oxidations might be expected in the oxidative scans of the composite complexes, corresponding to the respective 2e oxidations of the ($S_2C_3CH_3HCH_3$) and ($S_2C_3CF_3HCH_3$) ligands. However, on examining the anodic electrochemistry of the hybrids, only one dithiolium ion trace was observed, although the expected return wave indicative of the dithiolium ion reduction to the neutral radical was absent.

The oxidative signals are approximately half as intense as those discovered in the parent systems [M(S_2C_3RHR')$_2$],

Table 5.4 Cathodic Behaviour of $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ Systems in 0.5M Bu_4NBF_4/CH_2Cl_2 vs. Ag/AgCl

	$[M(S_2C_3CF_3HCH_3)_2]$		$[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$			$[M(S_2C_3CH_3HCH_3)_2]$	
M	$E°_{red}(1)$	$E°_{red}(2)$	$E°_{red}(1)$	Step (b)	$E°_{red}(2)$	$E°_{red}(1)$	$E°_{red}(2)$
Ni	-0.43V	-0.88V	-0.56V	-1.30V	-1.38V	-0.94V	-1.42V
Pd	-0.38V	-0.90V	-0.53V	-1.21V	-1.35V	-0.96V	-1.44V
Pt	-0.41V	-0.92V	-0.56V	-1.28V	-1.44V	-0.98V	-1.48V
	Parent A		The 'Hybrid'			Parent B	

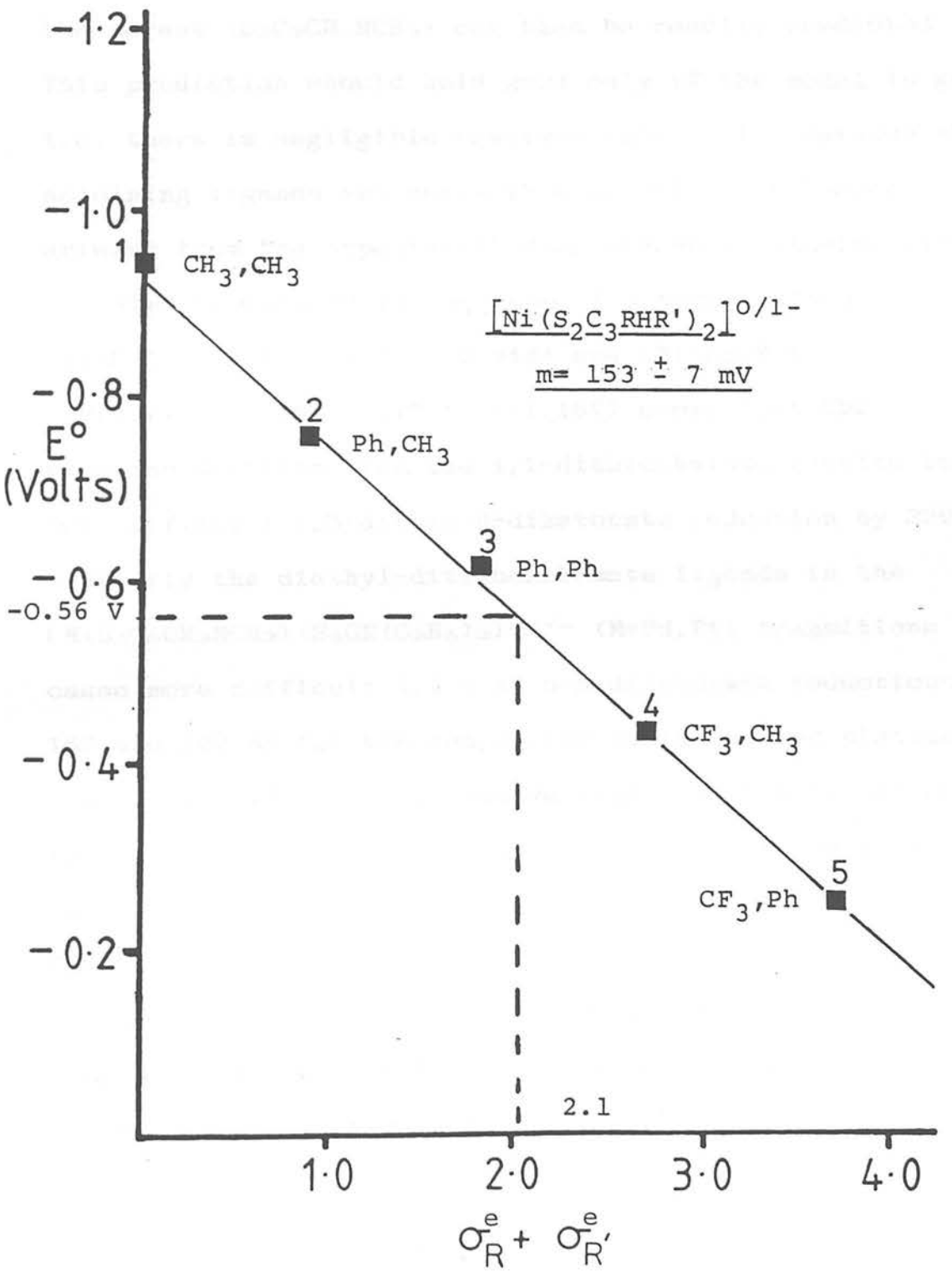
suggesting that only one ligand participates in a 2e oxidation. The incomplete voltammetric evidence makes it difficult to determine which 1,3-dithio-β-diketonate ligand participates in the oxidation, but the oxidation potential of the nickel-centred asymmetric complex, +1.35V, favours the involvement of the ($S_2C_3CH_3HCH_3$) chelate as expected. The oxidations of the Pd (+1.68V) and Pt(+1.61V) centred mixed complexes are unexpectedly difficult but these highly irreversible processes may be associated with a large overpotential, and there is also some evidence of electrode-tarnishing, so that it is not appropriate to consider the significance of these discrepancies at this stage.

5.5 The Assignment of Localised Ligand Reductions in Metal Bis-1,3-Dithio-β-Diketonates

Attempts to ascertain localised or delocalised electron acceptance in the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ reduction by direct interpolation of the first reduction potentials of the mixed complexes (Table 5.4), on the plot we constructed of Reduction potential of $[M(S_2C_3RHR')_2]$ versus Summed Electrochemically Derived Taft Inductive Parameter, provide a summed parameter of approximately 2.1 for all three mixed systems (Figure 5.6 displays this feature for the $[Ni(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ reduction). The inferred Taft value for these mixed complexes lies midway between the summed parameters for one ligand i.e. localised behaviour ($\Sigma(\sigma^*_{CF_3} + \sigma^*_{CH_3}) = 2.8+0 = 2.8$) and the summed parameter for two ligands i.e. delocalised behaviour ($\Sigma(\frac{1}{2}\sigma^*_{CF_3} + \frac{3}{2}\sigma^*_{CH_3} = 1.4$).

The major problem that arises in using this simplistic numerical approach is the assumption that the experimentally observed $[M(S_2C_3CF_3HCH_3)_2]^{0/1-}$ reduction, even if localised, is insulated from the effects of remote substituents. On the localised model, the problem with the data for all the symmetrical bis-complexes is that each individual redox-active ligand is found on a different binding site, as the partnering ligand also changes. Therefore the characteristic ligand reduction potentials must be corrected for this neighbouring substituent effect,

Figure 5.6 - Measurement of Summed Taft Parameter for $[Ni(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ Reduction.



in order to properly merge our data for symmetric and asymmetric bis-1,3-dithio systems.

Fortunately, our voltammetric examinations of the asymmetric hybrids [M(S_2C_3RHR')($S_2CNR''_2$)] have determined the Red(1) potentials for a series of 1,3-dithio-β-diketonate ligands. The Red(1) potential for the localised reduction of <u>any</u> 1,3-dithio-β-diketonate ligand opposite to the parent ($S_2C_3CH_3HCH_3$) can then be readily predicted. This prediction should hold good only if the <u>model</u> is good, i.e. there is negligible covalent interaction between the adjoining ligands and negligible inductive influence arising from the 'spectator' M($S_2C_3CH_3HCH_3$) binding site.

Thus comparison of the reduction potentials of [Ni($S_2C_3CH_3HCH_3$)$_2$]$^{0/1-}$ (-0.94V) and [Ni(S_2CN(i-C_3H_7)$_2$)($S_2C_3CH_3HCH_3$)$_2$]$^{0/1-}$ (-1.16V) shows that the electron-donation from the 1,1-dithiochelate results in a more difficult 1,3-dithio-β-diketonate reduction by 220 mV. Similarly the diethyl-dithiocarbamate ligands in the [M($S_2C_3CH_3HCH_3$)($S_2CN(C_2H_5)_2$]$^{0/1-}$ (M=Pd,Pt) transitions cause more difficult 1,3-dithio-β-diketonate reductions by 160 and 200 mV for the respective palladium and platinum-centred hybrids. The effective localised Red(1) values of the (S_2C_3RHR') ligands, obtained by removing the potential shift due to the 1,1-dithiochelate are summarised in Table 5.5.

Therefore voltammetric investigations of the mixed complexes [M($S_2C_3CF_3HCH_3$)($S_2C_3CH_3HCH_3$)] (M=Ni,Pd,Pt) with the first reduction conforming to the 'trapping' of the

Table 5.5 Calculated Red(1) Values for Isolated Reduction of (S_2C_3RHR') in [$M(S_2C_3RHR')(S_2C_3CH_3HCH_3)$]

M	R,R'	Effective Red(1)	$[M(S_2C_3RHR')_2]^{0/1-}$
Ni	*CH_3,CH_3	-0.94V	-0.94V
Ni	Ph,CH_3	-0.76V	-0.75V
Ni	Ph,Ph	-0.63V	-0.61V
Ni	*CF_3,CH_3	-0.50V	-0.43V
Ni	CF_3,Ph	-0.36V	-0.25V
Pd	*CH_3,CH_3	-0.96V	-0.96V
Pd	*CF_3,CH_3	-0.49V	-0.38V
Pt	*CH_3,CH_3	-0.98V	-0.98V
Pt	*CF_3,CH_3	-0.54V	-0.41V

electron on the chelate with greater electron-withdrawing capacity, ($S_2C_3CF_3HCH_3$), would theoretically lead to Red(1) values of -0.50V(Ni); -0.49V(Pd) and -0.54V(Pt). In contrast <u>completely</u> delocalised behaviour would result in Red(1) values of -0.69V(Ni); -0.67V(Pd) and -0.70V(Pt). Direct comparisons of the experimentally observed potentials for the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ reduction with those predicted localised and delocalised Red(1) values (Table 5.6 below) reveal good agreement between the localised Red(1) prediction and the observed experimental reductions.

<u>Table 5.6 Comparison of Predicted and Observed Red(1) Values for the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{0/1-}$ Reduction</u>

	Observed Red(1)	Predicted Red(1)	
M		Localised	Delocalised
Ni	-0.56V	-0.50V	-0.69V
Pd	-0.53V	-0.49V	-0.67V
Pt	-0.56V	-0.54V	-0.70V

If we assume the second reduction of the bis-1,3-dithio complexes, $[M(S_2C_3RHR')_2]^{1-/2-}$, to be localised on the ligand opposite the one involved in the first reduction, we can contrast localised Red(2) values for the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{1-/2-}$ reduction (i.e.

$[M(SacSac)_2]^{1-/2-}$) with predictions for reductions involving both ligands, i.e. delocalised. The theoretical and experimentally observed potentials are compared in Table 5.7 below.

Table 5.7 Comparison of Predicted and Observed Red(2) Values for the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{1-/2-}$ Reduction

M	Observed Red(2)	Localised Red(2) ($[M(S_2C_3CH_3HCH_3)_2]^{1-/2-}$)	Delocalised Red(2) (Predicted)
Ni	-1.38V	-1.42V	-1.15V
Pd	-1.35V	-1.44V	-1.17V
Pt	-1.44V	-1.48V	-1.20V

The similarities in the Red(2) values of $[M(S_2C_3CH_3HCH_3)_2]^{1-/2-}$ and the mixed complexes support the proposal that the second electron is 'trapped' on the $(S_2C_3CH_3HCH_3)$ ligand.

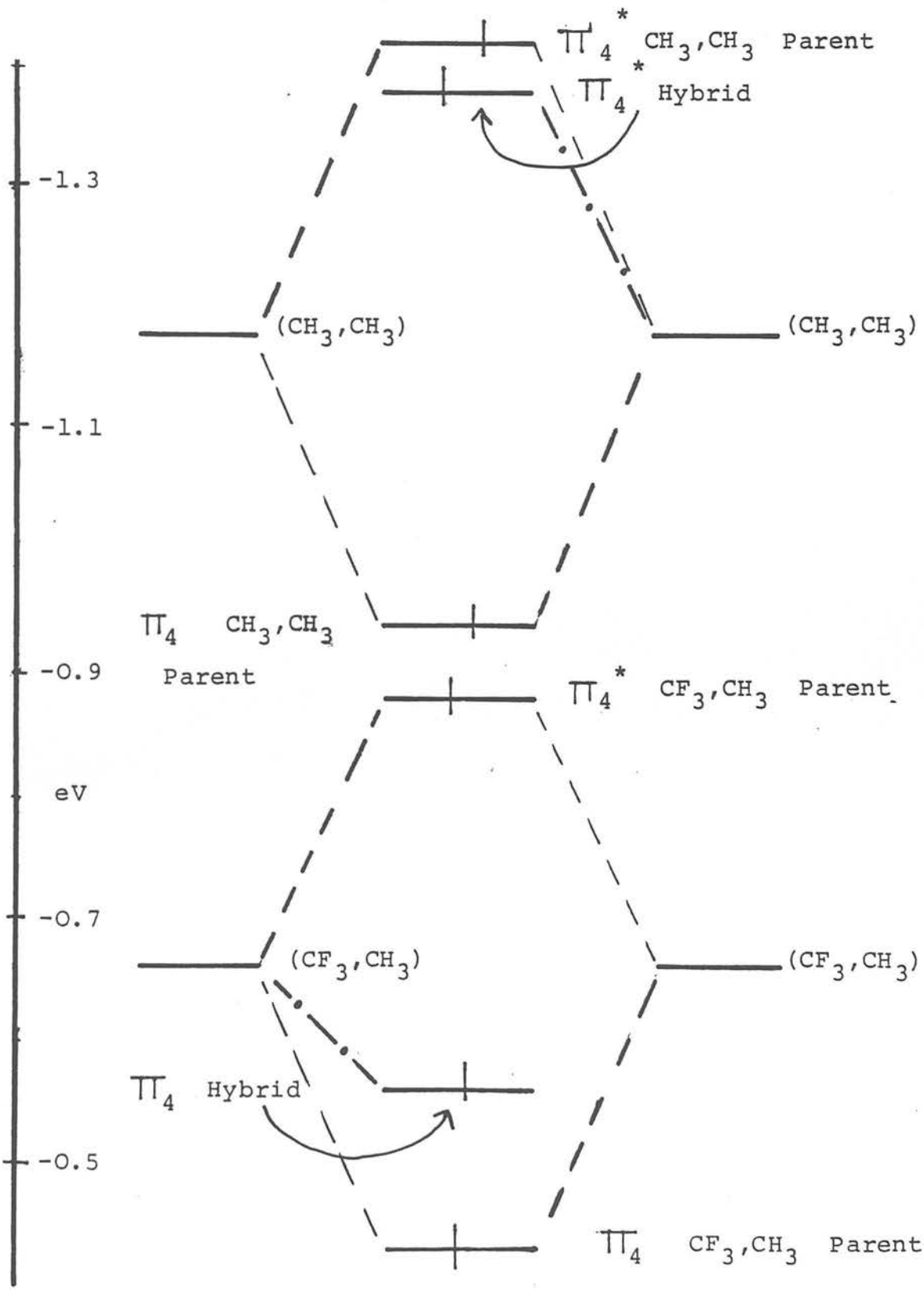
Moreover, our recognition that the two ligand-mediated reductions of $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ involve orbitals which are successively high in $(S_2C_3CF_3HCH_3)$ (Red(1)) and $(S_2C_3CH_3HCH_3)$ character (Red(2)), despite an approximate difference of 840 mV), suggests that the two ligand-based reductions of the $[M(S_2C_3RHR')_2]$ systems (Red(2) - Red(1)≈500 mV) are also similarly localised. A possible schematic MO summary of the

$[Ni(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{2-}$, $[Ni(S_2C_3CF_3HCH_3)_2]^{2-}$ and $[Ni(S_2C_3CH_3HCH_3)_2]^{2-}$ radical dianions is presented in Figure 5.7.

Thus our preliminary voltammetric studies, limited to the $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ asymmetric complexes (M=Ni,Pd,Pt), indicate that the successive ligand-based reductions of the mixed complex (and both $[M(S_2C_3CF_3HCH_3)_2]$ and $[M(S_2C_3CH_3HCH_3)_2]$) involve localised electron-acceptance. The first electron enters the CF_3-stabilised LUMO, with the second electron entering a different orbital (high in $(S_2C_3CH_3HCH_3)$ character) rather than being the second electron in the lower energy CF_3-stabilised LUMO.

Although our electrochemical investigations of the asymmetric $[M(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]$ systems strongly suggest localised electron-acceptance occurring in the two ligand-based reductions of the bis-1,3-dithio-ß-diketonates, further analogous studies are required to strengthen our proposal for predominant localised behaviour. Voltammetric examinations of the asymmetric complexes $[M(S_2C_3CF_3HCF_3)(S_2C_3CH_3HCH_3)]$ (M=Ni,Pd,Pt) would be most beneficial, due to the large difference that would exist between the predicted localised and delocalised Red(1) or Red(2) potentials (approximately 500 mV). However $[Pt(S_2C_3CF_3HCH_3)_2]$ has not yet been synthesised, and the corresponding Ni^{1s} and Pd^{1} complexes have only been obtained in very small yields by the Martin-Stewart template procedure. Thus, the preparations of the mixed systems $[M(S_2C_3CF_3HPh)(S_2C_3CH_3HCH_3)]$ (M=Ni,Pd,Pt) appear to

Figure 5.7 - Proposed M.O. Schemes for $[Ni(S_2C_3CF_3HCH_3)(S_2C_3CH_3HCH_3)]^{2-}$ and $[Ni(S_2C_3RHR')_2]^{2-}$ (R,R'=CF_3,CH_3; CH_3,CH_3)



be more plausible as a further electrochemical model, due to the parent complexes [$M(S_2C_3CF_3HPh)_2$] being readily accessible for Ni, Pd and Pt.

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Post Graduate Courses Attended

"Pulse Sequences and their Applications to Nmr Spectroscopy"

by Dr. G.A. Morris

"The Chemistry of Photographic Processes"

by Dr. L.A. Williams

"Homogeneous Catalysis"

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"Recent Advances in Electrochemistry"

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"Chemical Technology and Industrial Chemistry"

by Dr. A.J.S. Nicoll, Dr. L.H. Mustoe and Dr. R.S. Sinclair

University of Strathclyde Inorganic Club Conferences 1983, 1984, 1985.

Departmental and Research Seminars and Colloquia.

"Proceedings of the 2nd International Conference on the Platinum Metals", July 1984, Page D39.

REDOX-ACTIVE DELOCALIZED ORGANO-SULPHUR CHELATES OF NICKEL, PALLADIUM AND PLATINUM; ODD AND EVEN LIGANDS, AND HYBRID SYSTEMS

By Ian H. Anderson, G.A. Heath, and J.H. Leslie
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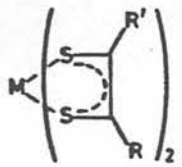
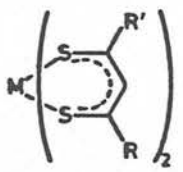
Voltammetric investigations in CH_2Cl_2 of many variously-substituted planar bis(dithio-1,3-diketonate) complexes $[M(S_2C_3RHR')_2$ (I; M = Ni,Pd, or Pt and R,R' = Bu, CF_3, Me, or Ph), including many new palladium and platinum complexes, confirm two reversible reductions in each case.[1] The successive one-electron transfers are found to be ligand-centred in $[M(S_2C_3RHR)_2]$ as in the '1,2-dithienes' $[M(S_2C_2R_2)_2]$(II), despite their difference in topology. An orderly dependence of reduction potentials on substituent influence (σ^*_R) is displayed by all such systems. In contrast, 1,1-dithiochelates such as $[M(S_2CNR_2)_2]$ accept an electron only at more negative potentials, with reduction of the metal centre.



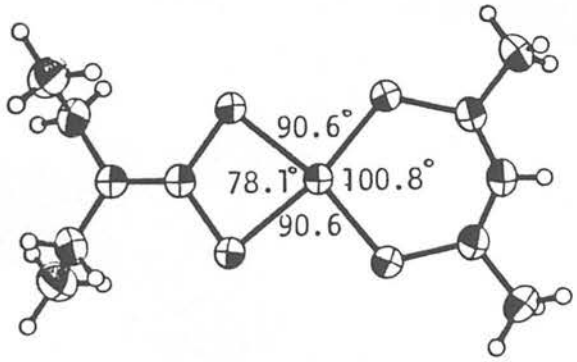
(I)



(II)

We have now prepared a range of hybrid (1,3-dithio)(1,1-dithio) complexes, typified by [M(SacSac)(dedtc)] (III;M=Ni,Pd,Pt), which make an interesting contrast with the 'isomeric' bis(1,2-dithio)systems.

The hybrid complexes gain additional stability from juxtaposition of mutually complementary π-acceptor and π-donor ligands. X-ray structural data define the strongly asymmetric nature of the planar MS_4 core (Figure).[2] The electrochemical behaviour corresponds to isolated one-electron reduction of the SacSac ligand, and electronic spectra show recognizable separate M(SacSac) and M(dedtc) chromophores.



(III, M = Ni)

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