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# DEVELOPMENTS IN THE ANALYTICAL GAS CHROMATOGRAPHY OF METAL DIALKYLDITHIOPHOSPHATE COMPLEXES

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## INTRODUCTION

The gas chromatographic analysis of metal-containing compounds has been a small but reasonably active field for about 25 years. Analyses cover such areas as organometallics, metal complexes, and compounds such as hydrides and halides. Reviews of the field may be seen in the books by Moshier and Sievers (1), Guiochon and Pommier (2) and Crompton (3), as well as the papers by Uden and Henderson (4) and Rodriguez-Vazquez (5). Metal chelates are of specific interest because of the volatility which they may impart to the metal. Many chelating ligands have been investigated, most with either two or four coordinating sites to the central metal. Most of these tend to be based on acetylacetone-type models, with various different substitutents on the ligand providing different volatility characteristics to the derivatised metal (such as the trifluoro group giving enhanced volatility to acetylacetone complexes). Thus the ligand may coordinate to the metal as an O, O- or O, S- chelate. Dithiocarbamates (6) and dithiophosphates (7) coordinate through two sulphur atoms.

Tetradentate ligands have been constructed and successfully applied to GC of metals. The ligand is often built up around an ethylenediamine or propylenediamine group which provides two nitrogen coordinating sites, with either two oxygen or two sulphur atoms on the appended side chains providing the two further coordinating sites (see for example Patsalides etal. (8) ). Most of these tend to be 'wrap-around' ligands. Few examples of ligands which possess a vacant hole in a cyclic structure suitable for GC of metals have been reported. The porphyrin complexes, containing the cyclic tetrapyrrole ring and coordinating through four nitrogen atoms have been successfully gas chromatographed (9-11). Their very high thermal stability combined with low volatility mean high temperatures were necessary in the GC experiment. The GC of axially-derivatised chelates proved to be more favourable than that of bare (unshielded) metalloporphyrins. Hyperpressure chromatographic techniques, now seeing a resurgence of interest, were first developed for analysis of porphyrin compounds (12) GC of metals with hexadentate ligands has apparently not been reported.

Metal dithiophosphate GC has been developed by Cardwell etal. The first report was in 1974 (7). Successful analysis of Ni, Zn, Pd, Pt, Cr and Rh was reported with a number of chelates indicated as not being suitable. The GC characteristics on packed and capillary columns and also with photometric detectors have been described (13, 14). Sucre and Jennings reported similar work on capillary columns (15).

The present paper will discuss the GC of a wider range of dithiophosphates, with different metals and a wider range of alkyl side chains. Preliminary experiments on mixed ligand species will be outlined.

## EXPERIMENTAL

### Gas Chromatography

GC analyses were carried out on a Hewlett-Packard 5790 instrument equipped with both packed and capillary column injectors. Flame ionisation detection was used for most work. A Hewlett-Packard reporting integrator, model 3390 and Perkin-Elmer chart recorder provided output recording. Scientific Glass Engineering injection syringes were used. Nitrogen carrier gas for all GC studies was used. Chelates were dissolved in either hexane or dichloromethane.

### Preparation of ligands and chelates

Dialkyldithiophosphoric acid ligands were prepared by standard methods, by addition of the appropriate alcohol, ROH, to $P_2S_5$ followed by gentle heating;

$$4ROH + P_2S_5 \longrightarrow 2(RO)_2PS(SH) + H_2S$$

The $H_2S$ is boiled off and the alcoholic solution was treated with the metal salt to give the metal chelate. The complexation step proceeds much faster for shorter alkyl chain ligands. Thus for R = methyl, ethyl etc the solution takes on the purple (for nickel) colour immediately, but for R = isoamyl, t-butyl etc the solution only slowly adopts a purple colour. Likewise the $P_2S_5$ dissolves more slowly in the alcohols with larger R groups. The range of alkyl side chains incorporated into the ligand include those in Table 1, in which the boiling points of the alcohols are also listed.

Other alcohols attempted included cyclohexanol, t-butanol, 1, 3-propanediol and allyl alcohol (2-propen-1-ol). These latter alcohols gave products which did not GC successfully, and were presumed to decompose. The last two imparted distinctly purple coloration to the solution but the complex could not be isolated and purified. The longer side chain products were obtained as oily products. Very few reports of diols used for the alcohol group have appeared (16). The Table also includes the range of metals incorporated into the complexes. The Cu(II) chelate (from $CuSO_4.6H_2O$) was not obtained as a solid product. The solution was a yellowish brown colour. Wasson (17) was also unsuccessful in isolation of the Cu (II) product, suggesting the subsequent formation of Cu (I) ( $(RO)_2$ $PS_2$). The solid Co chelate was studied by thermogravimetry; a weight loss of ca 40%, commencing at about 180°C, occurred.

Synthesis of the vanadyl (oxovanadium (IV) ) complex, using ammonium metavanadate $(NH_4)$ $VO_3$ in a similar manner to that of Dilli (18) for his tetradentate complex, proceeded through a number of intermediate coloured states. The very pale yellow ligand solution became initially pink when the metal was added, deepening to a dull reddish-pink. A brown/orange colour then developed and turned light green, darkening to an aqua blue. A second preparation, under argon to exclude air, followed a similar sequence without the green colour. The solution turned green after standing for several weeks in a stoppered flask. Wasson (17) indicated the oxovanadium (IV) complex to be blue. The solution was sampled directly for GC study, with the chelate not being crystallised out of solution. Samples of chromatographed complex were collected by stripping the polymer coating off the capillary column, and pushing the stripped column through the detector to the cool external air. Complex was observed to condense on the inside surface from which it could be washed out. The collected fractions had the same colour as the injected solution, confirming that the compounds were successfully gas chromatographed.

| | **RETENTION INDICES** | |
|---|---|---|
| **Nickel complexes** | | alcohol B.P. (°C) |
| dimethyl | 2110 | 64.6 |
| diethyl | 2320 | 78.5 |
| diisopropyl | 2320 | 82.4 |
| (ethyl) (isobutyl) | 2545 | |
| dipropyl | 2630 | 97.4 |
| disecbutyl | 2665 | 99.5 |
| diisobutyl | 2740 | 108 |
| dibutyl | 2970 | 117.3 |
| diisoamyl | 3150 | 128.5 |
| **metal bis(diethyldithiophosphates)** | | |
| Cu (II) | 2065 | |
| Zn (II) | 2250 | |
| Ni (II) | 2320 | |
| Co (II) | 2420 | |
| V(IV) O | 2460 | |
| Pd (II) | 2420* | literature values |
| Pt (II) | 2460* | |
| tris complex | | |
| Cr (III) | 3050 | |

TABLE I Retention indices for various metal dialkyldithiophosphates.

## RESULTS

### Retentions of Metal dithiophosphates

Both relative retention differences resulting from varying alkyl substituents on the ligand, and the retention variations when the metal is changed were studied.

Effect of alkyl substituents. The longer alkyl chain ligands usually produce better (more symmetric) peak shapes for the chelate. The lack of symmetry is often observed as a tailing of the peak, which may be due to adsorptive interaction or possibly a non-linear isotherm. It is noted that the shorter chain complexes tend to show poorer solubility in non-polar solvents (eg. hexane). This might result in similar poor partitioning between the gas and liquid phases onthe column, though this would probably be expected to lead to fronting of the peak. Similar observations to the above have been made for GC of various metal dithiocarbamates. The authors attributed this effect to shielding of the nitrogen for longer alkyl substituents (19). Figures 1 & 2 illustrate typical gas chromatographic traces. Retention indices are listed in Table I. For the nickel complexes, plots of number of carbon atoms in each alkyl group against retention index are given in Figure 3. It can be seen that the straight-chain species – an homologous series – all essentially lie on a straight line, although the methyl seems to be anomolous. The isoalkyl series also

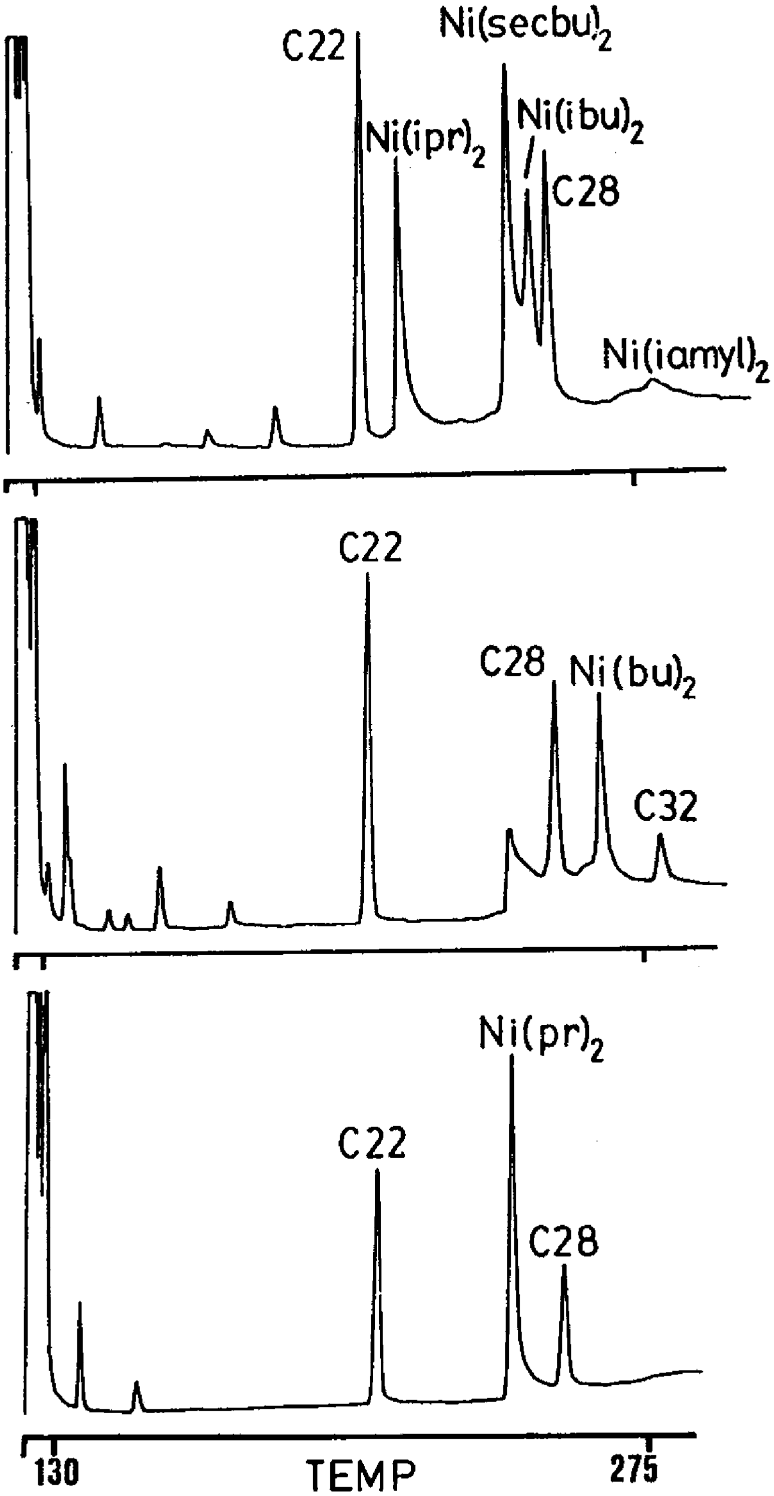
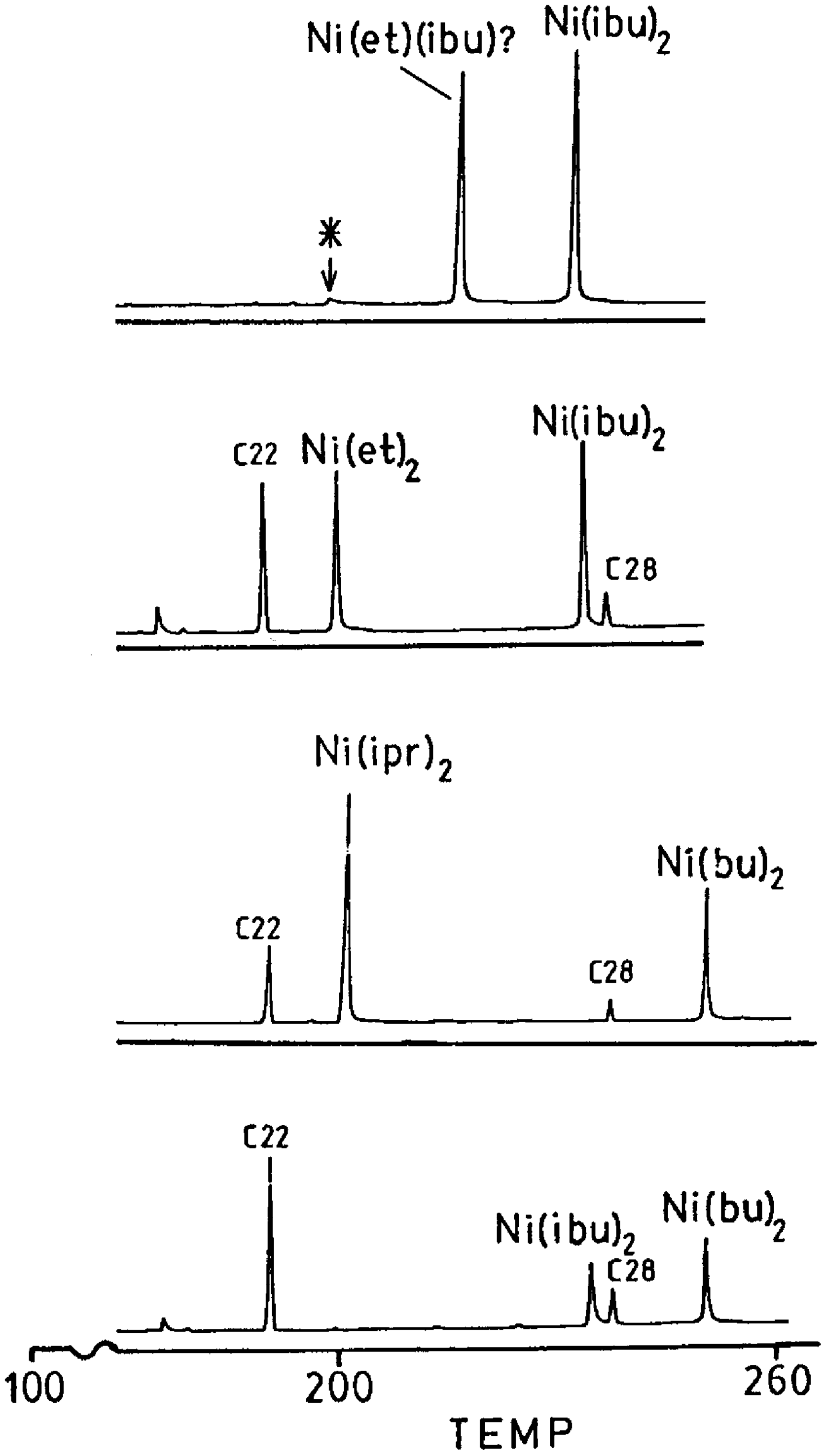


Figure 1A Chromatograms of mixtures of nickel chelates on a packed stainless steel column, 2% OV-101 on Chromosorb WHP, with coinjected C22 and C28 alkanes. Temperature programming from 130°C to 275°C at 5°C. $\text{min}^{-1}$ Abbreviations correspond to alkyl group on the ligand.



1B Capillary column studies of some chelate mixtures.

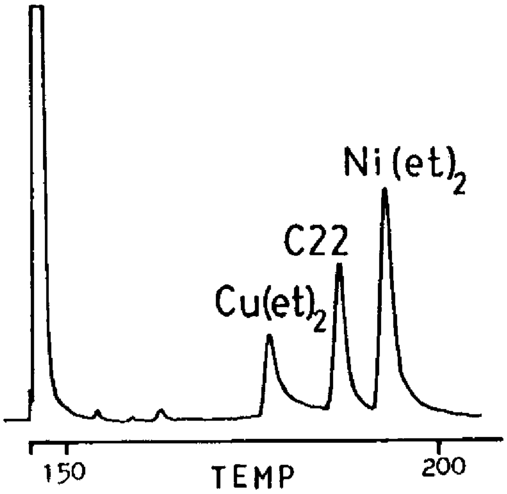


Figure 2 Chromatogram of Cu and Ni diethyldithiophosphates. Column as Figure 1, temperature programmed from 150°C to 200°C at 5°C. $^{m}$in-1.

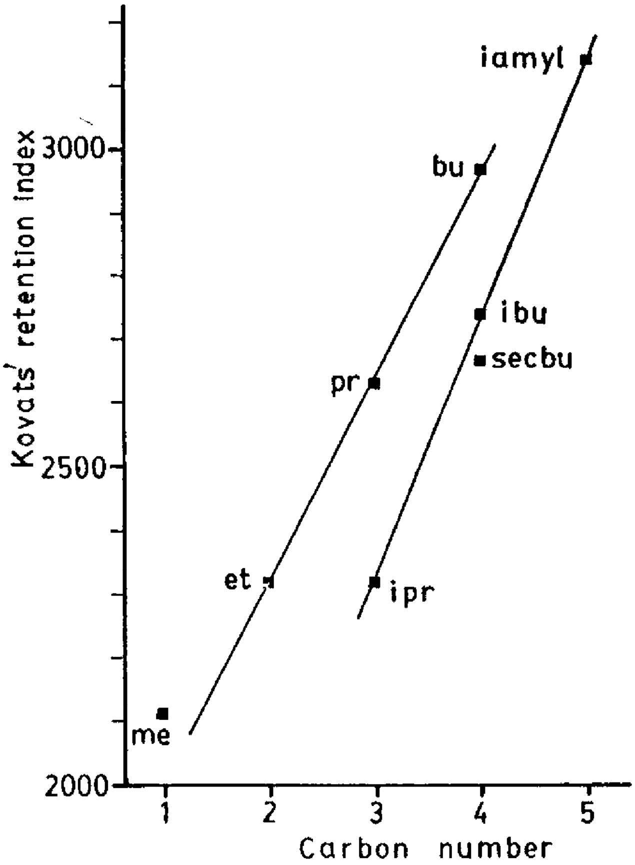


Figure 3 Retention index plots for various nickel complexes on OV-101 packed column (indices calculated under temperature programmed conditions), against number of carbon atoms in each alkyl side chain (indicated by abbreviations).

delineate a straight line, though of slightly greater slope than that of the n-alkyls. It is interesting to note that the retention different between members of the n-alkyl series is the same as that between the isopropyl and secbutyl complexes. Thus the phenomenon which dictates differences in retention for the n-alkyls probably also operates to produce the isopropyl/secbutyl difference.

If retention data are plotted against boiling point of the appropriate alcohol ûsed to prepare the ligand, the data fall almost uniquely on straight line; only isopropyl and iso-

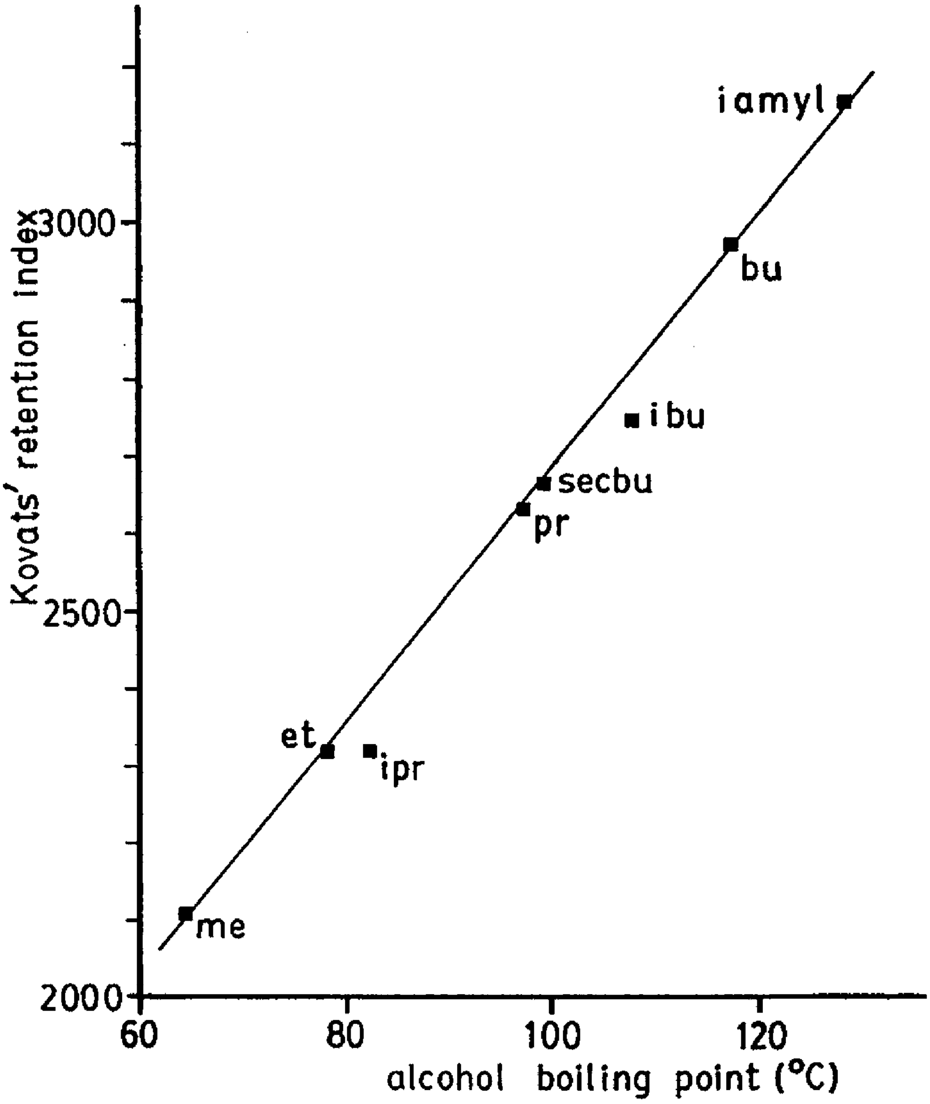


Figure 4 Retention index plot against boiling point of the alcohol used to prepared each chelate as appropriate.

butyl deviate. This suggests that the lipophilic properties of the alkyl part of the alcohol, on which the boiling points may be correlated, determine retention of the complex also, although the alcohols must be considerably more polar. presumably the enhanced solubility of the longer organic chain in the stationary phase, coupled with increasing molecular mass of the complex, contribute as well. In fact, retention data (indices) of alcohols when plotted against boiling point, indicate an approximate linear relationship.

Effect of central metal. For different metals, chelated with the diethyldithiophosphato ligand, the order of retention is comparable with that reported for other chelating systems in GC. Retention data are listed in Table I. A case in point is the metalloporphyrins (9), as the aetioporphyrin or octaethylporphrin complex, which showed an order of:

$$Zn(II) < Cu(II) < Ni(II) < V(VI) < Co(II) < Pd(II) < Pt(II)$$

The orders Ni< Pd< Pt and Cu<Ni<Co have been observed with other chelating ligands.

Precisely what parameter is responsible for determining the observed retention has apparently not been elucidated. Clearly volatility (vapour pressure) and solubility in the stationary phase will play major roles in defining a chelate's partition behaviour on the column. Further definitive study using techniques which may shed light on these and any other possible physical parameters must be undertaken. Some studies on different chelates in GC have resorted to doping of the carrier gas with ligand vapour prior to the injection zone of the GC instrument, this being done to overcome undesirable decomposition either in the injector or on the column. This has not been investigated for the dithiophosphates, but may be instructive for such complexes as the Zn one, where rather poor chromatography is often observed (13). This doping may also reveal whether decomposition does take place, since suppression of decomposition would be indicated by increases in chelate recovery (peak height) at the detector. It should be noted, however that decomposition has not been suspected nor indicated for these compounds in any of the GC trials.

Favourable chromatography of the Cr(III) chelates can be seen in Figure 5, when the pure individual chelates are analysed. In preparation of running a complex mixture derived from the use of two alcohols (EtOH, iBuOH via reaction Procedure I), a sample containing just $Cr(et)_3$ and $Cr(ibu)_3$ was injected. The unusual behaviour exhibited by this mixture may be seen in Figure 5. The two peaks appear to be mutually skewed towards each other, and at first might be thought to be due to some type of dynamic interchange or exchange phenomenom, since this general peak profile behaviour has been observed in situations where on-column reactions occur. These involve the conversion from one compound into another, and if the process is reversible, a coalescence may occur (similar to NMR peak coalescence). This has been dramatically illustrated by ourselves (20) for thermal interconversion of conformers, and also for stationary phase-mediated enantiomerisation (21). However, for the chelates it is difficult to postulate the 'chromatographic reactor' arising to explain the peak shapes, since the $Cr(et)_3$ species cannot directly convert into the $Cr(ibu)_3$ species once the column has effected separation of two (the chromatographic reactor is a continuous conversion process). Unusual isotherms apparently do not exist – each compound chromatographs well (upper traces). If some of the ethyl complex were irreversibly adsorbed on the column and were 'released' with passage of the isobutyl complex over it, behaviour as observed may result. But this mechanism appears unlikely.

When a complex mixture of chromium complexes, derived from the use of two alcohols initially, was analysed, the result was, predictably on the basis of the foregoing dis-

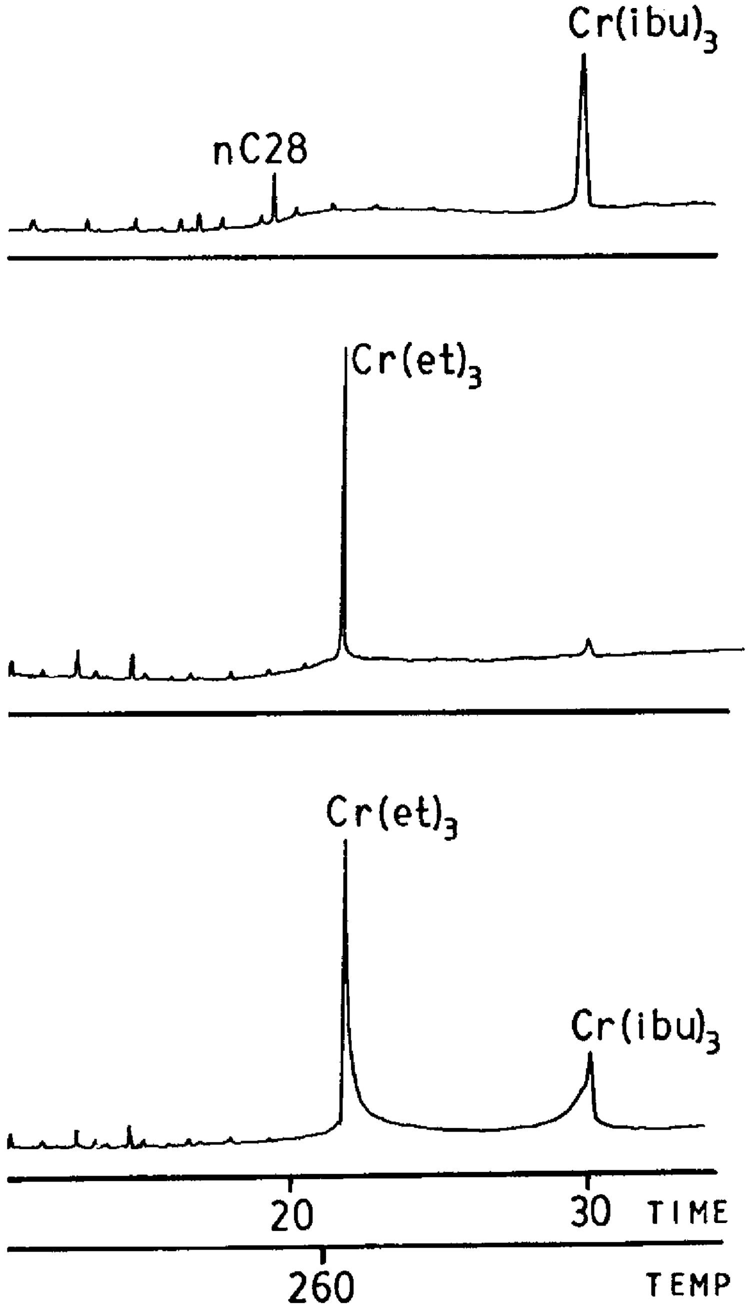


Figure 5 Chromatograms of chromium complexes with diethyl and diisobutyldithiophosphate, using a 6m OV-101 flexible silica column and splitless injection. Temperature programmed at 5°C. min$^{-1}$ from 100°C to 260°C.

cussion, rather anomalous also. Although the separation of the terminal (ie $Cr(et)_3$ and $Cr(ibu)_3$) peaks was expected to be about $R_s$ ca. 15, and thus able to accommodate many mixed ligand species between them, the result was a broad conglomerate of poorly resolved peaks which could not be reconciled with the expected pattern. Clearly, interchange or a mechanism similar to that above must result in the lack of resolvability of the mixture's components.

Analytical studies using metal chelate gas chramatography. The potential applications (analytical) of metal chelate GC are relatively limited, and not too many have appeared in the literature. Undoubtedly this is due to

i) the unique and limiting physical requirements placed upon the chelating system ie. thermal stability of a neutral complex with quantitative and easy formation.
ii) competition with other well established methods for metal determination – AAS, AES, electrochemical, HPLC, conventional methods etc.

Thus determination of chromium in hair and standard materials via its trifluoroacetylacetonate complex, determination of nickel, copper and vanadium in fuel oils and sediments (22) and so forth have received attention. Organometallic compound GC is well appreciated, mainly through its prime example of lead alkyl analysis. This area is reviewed in the recent book by Crompton (3). The requirement of derivatisation may mitigate against use of metal chelate GC. If the metal is in a form suitable for GC (eg the Mn carbonyl compound in petrol, lead in petrol etc.) the use of GC is more attractive. The dithiocarbamates have been used for metal determination in sediments, after derivatisation (23), and dithiophosphates for Zn determination (24). Our experience with Cu analysis using solvent extraction of the metal from standard $Cu^{2}+$ solutions and from a prepared alloy solution using diethyldithiocarbamic acid, following the procedure given in Vogel's text (25) gave satisfactory results although precision was not as good as for the spectrophotometric monitoring of the chelate's absorption intensity in the extracting organic phase. Substitution of diethyldithiophosphoric acid in the above procedure did not prove successful. Given the relatively low profile of metal complexes in analytical GC of 'real' samples, prospects for the dithiophosphates in this field do not appear to be strong.

It may be appropriate to recognise the ever increasing role of HPLC in metal chelate and organometallic analysis. Not relying on the often restrictive requirement of volatility, many types of compounds have been routinely and successfully studied. In fact, many synthetic inorganic groups depend upon HPLC as part of their routine 'quality control' of reaction mixtures, which is a strong vote of confidence for the method. Reviews of this field are available (26).

The silicon derivatives of suites of naturally-occurring porphyrins have been successfully applied to GC and GCMS studies in order to obtain data on the range and types of porphyrins in oil and shale samples (27). Aluminium derivatisation holds similar potential, but results in greater retention volumes for the product metalloporphyrins. Direct injection of the nickel and vanadyl fractions was not attractive, due to the high temperatures and poor resolution associated with their GC.

## Ligand exchange and mixed ligand complexes

Mixed ligand complexes arises in three possible ways:

procedure I the use of a mixture of alcohols in the initial preparation of the phosphorodithioic acid (RO) (R'O) PS (SH), with subsequent reaction of the reaction soup with the metal salt (Figure 6).

### PREPARATION OF NICKEL COMPLEXES

i) **Ligand solutions**

$$\begin{array}{rcl}
\mathrm{R-OH + P_2S_5} & \longrightarrow & \mathrm{(RO)_2PS(SH) = A{-}H}\\
\mathrm{R'-OH + P_2S_5} & \longrightarrow & \mathrm{(R'O)_2PS(SH) = B{-}H}\\
\mathrm{R{-}OH + R'{-}OH + P_2S_5} & \longrightarrow & \left.\begin{array}{l}\mathrm{(RO)_2PS(SH) = A{-}H}\\ \mathrm{+\ (R'O)_2PS(SH) = B{-}H}\\ \mathrm{+\ (RO)(R'O)PS(SH) = C{-}H}\end{array}\right\}\ \mathrm{I}
\end{array}$$

ii) **Complexes**

$$\mathrm{A{-}H + NiCl_2 \longrightarrow [Ni(A)_2]}$$

$$\underbrace{\mathrm{A{-}H + B{-}H + C{-}H + NiCl_2}}_{\mathrm{I}} \longrightarrow \mathrm{[Ni(A)_2] + [Ni(A)(B)] + [Ni(A)(C)]}$$
$$\mathrm{+\ [Ni(B)_2] + [Ni(B)(C)] + [Ni(C)_2]}$$

Figure 6 Summary of preparative procedures of ligands and chelates including mixed chelates (equations not balanced for brevity).

procedure II preparation of individual dialkyl acids followed by mixing two or more acid ligands together before addition of the metal salt

procedure III employing ligand exchange to substitute one alkyl substituent on a complex with a different one:

A : $\mathrm{M(S_2P(OR)_2)_2 + R'OH \longrightarrow M(S_2P(OR)(OR'))_2}$ + etc.

B : $\mathrm{M(S_2P(OR)_2)_2 + M(S_2P(OR')_2)_2 \longrightarrow M(S_2P(OR)(OR'))_2}$ + etc;

Whilst the first two methods should be straight forward, with potentially predictable heterogenous mixtures of a range of products dependent upon the valency (2+ or 3+ etc.) of the metal and the number of alcohols employed (I) or complexity of acid ligands (II) used (provided the products statistically obey the range of possibilities), the third procedure is perhaps more problematical, dependent upon many factors which need to be satisfied in order to obtain a mixed product. Transesterification of the acid ligand, ie.

$$\mathrm{(RO)_2PS(SH) + R'OH \longrightarrow (RO)(R'O)PS(SH) + ROH}$$

has been reported by Wingefors (28) to produce an unsymmetric ligand. Removal of ROH as the reaction proceeds will force the reaction forward (R=small chain, <hexyl; R'> hexyl for this to be successful). The methylheptyldithiophosphoric acid was used in solvent extraction studies, although the transesterification product was reported to be rather impure. Whether this protocol of transesterification would succeed for ligands already complexed to metals has not yet been evaluated or mechanisms elucidated, although the scrambling of ligands has been referred to (29).

Recently, ligand exchange of antimony (III) complexes with nickel salts was reported (30). This is an example of procedure IIIB above. The THF solution took on a characteristic colour indicative of the purple nickel complex. Yields of the order of 50% were indicated, and pseudo-first order rate constants tabulated. It was concluded that the rate was dependent upon the alkyl group's inductive effect, but not on the steric effect. The smaller and less branched alkyl groups had faster rates of ligand exchange via an $S_N2$ mechanism of chloro attack at the Sb with subsequent loss of a ligand molecule. Ligand exchange from one nickel to another, in the absence of a small anionic group would have to proceed via a different mechanism. Solution mixtures of nickel complexes appear not to undergo ligand exchange in our experience, however elevated temperature work has not been investigated.

In work with zeolites, hydroxy groups on the catalyst surface can act as the exchanging 'alcohol' group following the procedure IIIA type reaction. An alternative, favoured interaction involving basic $A10_4^-$ sites was also proposed. Acidic substrates tend o degrade the nickel complex – an observation we have also made for silica column chromatography with dichloromethane of certain nickel complexes. The zeolite, during preparative anchoring reactions, adopts the purple colour of the complex, but loses much of its hue when dried. Wetting the solid restores the coloration.

In a recent HPLC study of metal dithiophosphates (31), Co(III) and Cr(III) tris chelates were investigated for ligand exchange. The labile Co(III) complexes exchange more rapidly than the more inert Cr(III), although the latter exhibit exchange at elevated temperatures. Apparently all of the anticipated products were observed after the exchange process occurred. These workers studied reactions of type procedure I and procedure IIIB.

Ligand exchange can be readily observed when nickel salt is added to a solution of the zinc complex in, eg chloroform (solution goes from clear to purple). Sabot and Bauer (32) indicate exchange between Co(II) $L_2$ and $Ni^{2+}$

The few studies thus far attempted on the GC of mixed ligand complexes were performed for methyl/ethyl, ethyl/isobutyl and ethyl/propyl systems. The data are perhaps too limited to come to general conclusions, but the observations certainly indicate the formation and separation of the mixed species. The ethyl/isobutyl trials were from EtOH/iBuOH starting materials (ie procedure I). This resulted in a small peak for $Ni(et)_2$, with large (ca. same size) mixed ligand and $Ni(ibu)_2$ peaks. The choice of the two starting alcohols was made on the basis of the anticipated favourable separation of the peaks without too great a retention difference. Repeating procedure I with EtOH and MeOH gave large $Ni(me)_2$ and mixed ligand peaks, with a very small $Ni(et)_2$ peak. This experiment was qualitatively similar to the previous one above, however the results in terms of relative abundances of the various products are different. In the former, the $Ni(et)_2$ peak was small (for ethyl being the smaller alkyl group) but in the latter one the $Ni(et)_2$ is also small abundance with the ethyl being the larger of the two alkyl groups (me and et). This suggests that the trend is not regular for the two systems. Note that whilst about 6 peaks were expected for this mixture of two starting alcohols, only three were seen and even then one was very small.

A mixture of ligands $(me0)_2PS(SH)$ and $(et0)_2PS(SH)$ was taken as in procedure II. Two peaks resulted, with three being expected. The mixed ligand product was not evident, and the two peaks seen had retentions precisely the same as the symmetric bis complexes only. Using the ethyl and propyl acid ligands again in procedure II, the mixed ligand product was observed but it was of considerably lower abundance than the terminal peaks.

Figure 7 summarises some example chromatograms for the above investigations.

Since complete product ranges have been recently reported (31) for tris Co(III) and Cr(III) mixed ligand complexes, the question remains as to why the expected complexity has not been reproduced here, for the bis Ni complexes. Trials with varying relative amounts of alcohols (or acid ligands) and sampling the reaction mixture at different lengths of time did not indicate any quantitative or qualitative changes inconsistent

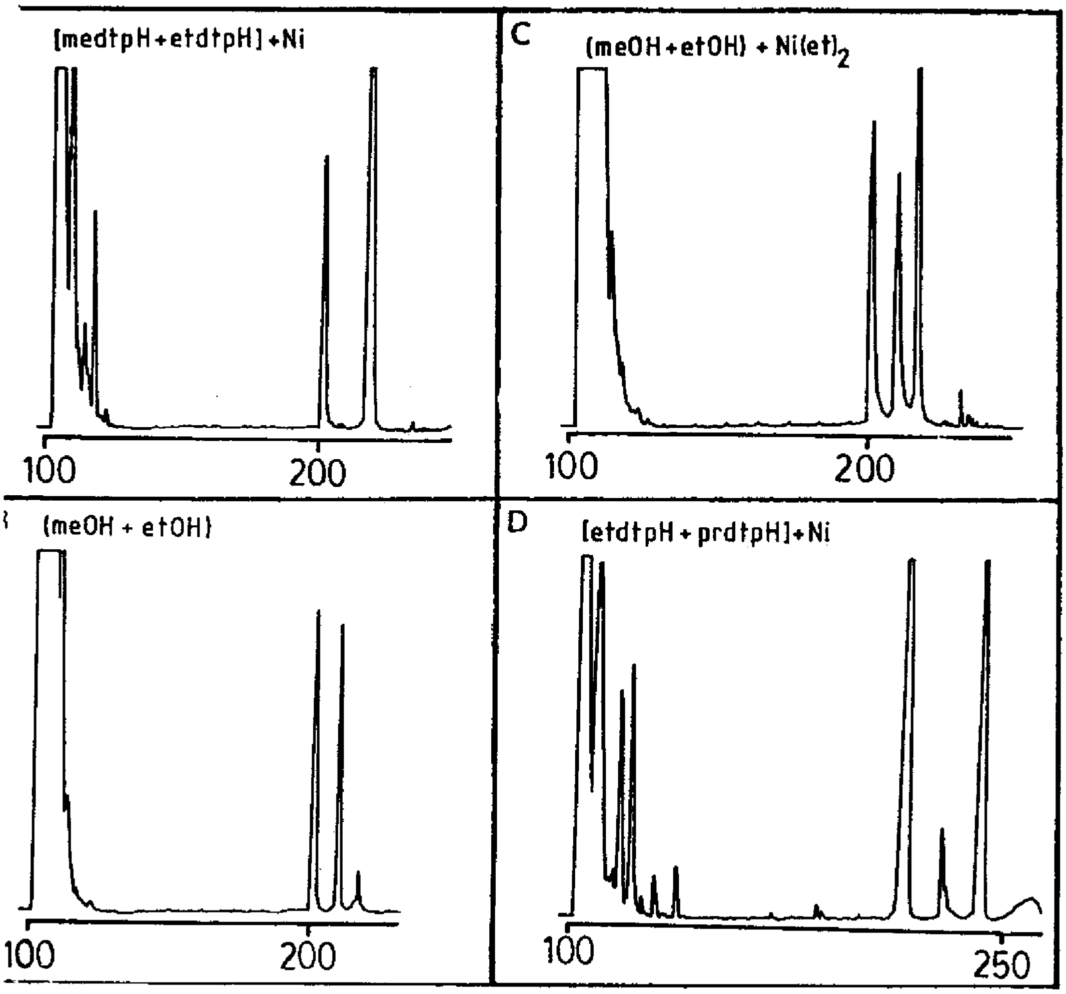


Figure 7 Chromatograms of mixtures of mixed ligand preparations with nickel.
A : procedure II type; dimethyl and diethyl
B : procedure I type; methanol and ethanol
C : solution as in B, but with added diethyl chelate
D : procedure II type; diethyl and dipropyl
Capillary column as in Figure 5, temperature programmed 100°C to 260°C throughout.

with those above. Procedure II was the one considered most likely to give good statistical distributions; further study will be needed before reasons for failure in this can be understood. Further experimentation relating to the distributions of mixed alkyl acid ligands generated from different alcohols will be beneficial. Gas chromatographic monitoring of these intermediate mixtures will show if the scrambling or generation of mixed alkyl ligands reflects the reactions which should be taking place. Sampling the crude product solution for GC usually leads to peaks appearing just after the solvent. Their elution is accompanied by a definite green glow imparted to the flame of the FID, which must correspond to the elution of a phosphorus compound into the flame much as is employed in the flame photometric detector, which is due to emission from HPO*. Figure 8 shows the occurrence of three peaks eluting just after the solvent in a mass spectrometric experiment (GCMS). The spectra of the three peaks may be seen in Figure 9. These correspond to various phosphorodithioic acids – the O, O, S-trimethyl, O, S-dimethyl-O-ethyl, and O, O-diethyl-S-methyl esters for the $M^+ = 172$, 186 and 200 m/z compounds respectively (this is also their relative retention order). This certainly indicates the presence of the mixed alkyl acid ligand in the mixture. Presumably the absence of the O, O, S-triethyl analogue means that all the compounds are S-methyl esters. Mass spectra of the nickel chelates in the same GCMS trial are given in Figure 10. Since this is the product of a procedure I type reaction, it is uncertain whether the mixed ligand product is either

$$\mathrm{Ni((meO)(etO)PS_2)_2} \quad \text{or} \quad \mathrm{Ni((meO)_2PS_2)((etO)_2PS_2)}.$$

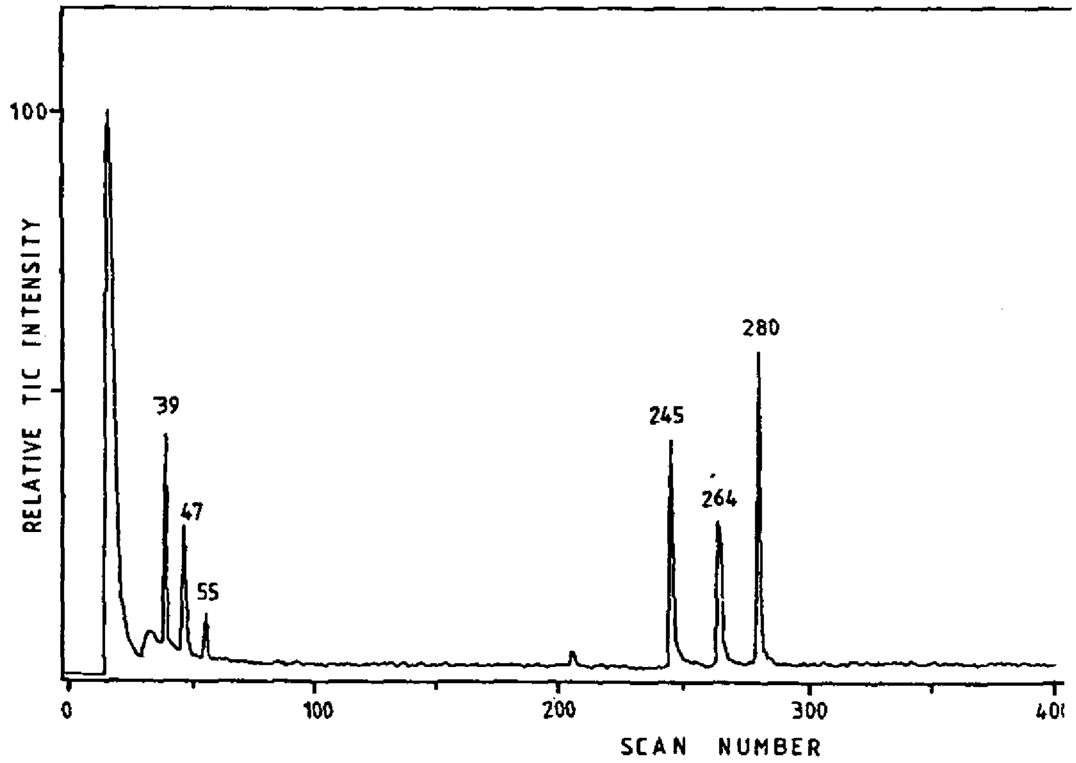


Figure 8 GCMS analysis of mixture as in Figure 7C. 70eV ionisation potential using electron impact.

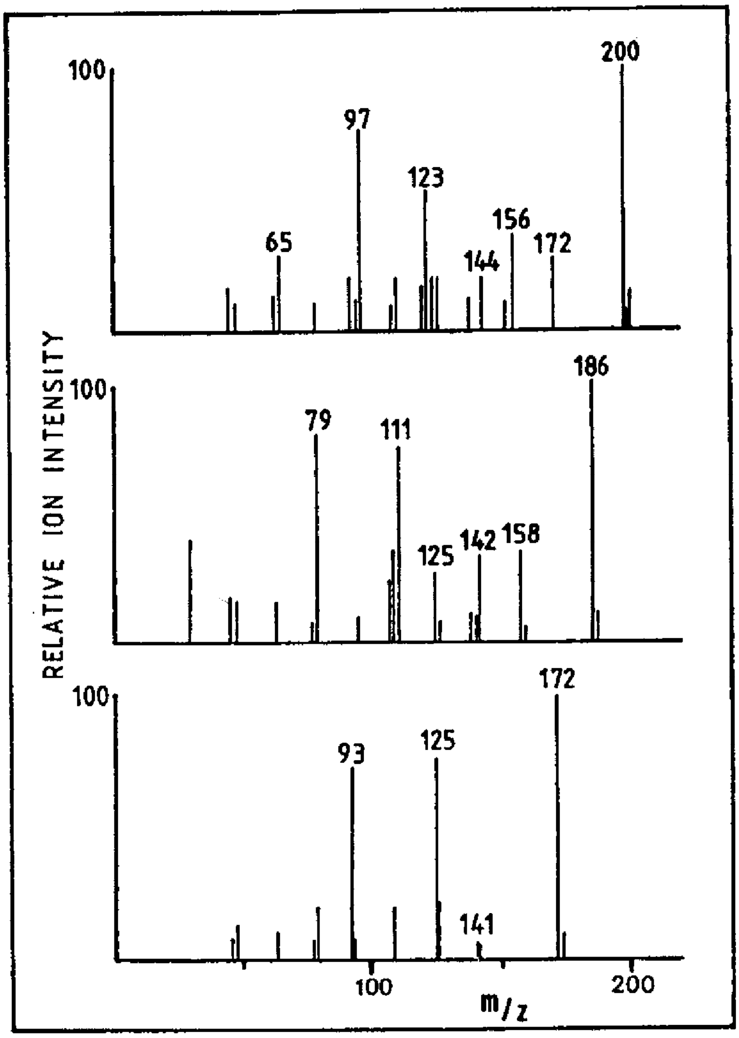


Figure 9 Mass spectra of the early eluting peaks shown in Figure 8. $M^{+} = 172$, 186 and 200 m/z for peaks with scan numbers 39, 47 and 55 respectively. For identity of peaks, refer to text.

Any other possible products have been ruled out on the basis of the complex's retention time, which is close to midway between those of the symmetric terminal complexes. Thus we would expect it to have two ethyl and two methyl groups. The MS fragmentation patterns were closely scrutinised but did not appear to offer any firm confirmation supporting either of the two possibilities.

HPLC studies of metal dithiocarbamates have indicated ligand exchange phenomena. Lehotay etal (33) indicated that both ligating groups on the nickel metal exchange with both on the copper metal in some sort of concerted reaction. Through a secondary reaction the nickel complex thus produced exchanged with original nickel complex to give a mixed product. It is improbable that this interchange occurred exclusively in the HPLC column – most probably the exchange took place in the solution prior to injection. In GC studies of the dithiocarbamates, no mixed species have been reported to the author's knowledge.

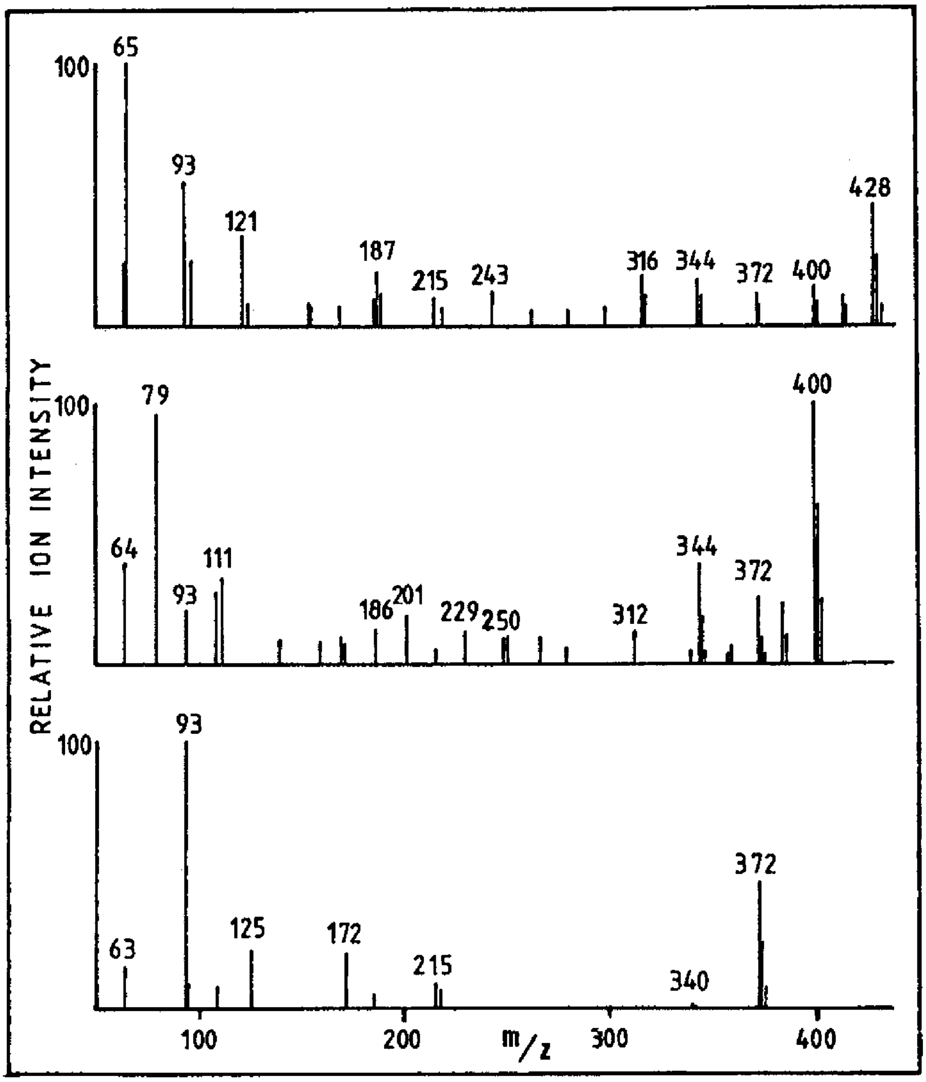


Figure 10 Mass spectra of the later eluting peaks of Figure 8. $M^{+}$ = 372, 400 and 428 for peaks with scan numbers 245,264 and 280 respectively, corresponding to bis(dimethyl), (dimethyl) (diethyl)* and bis(diethyl) nickel complexes.

Lack of fragment ions in the bis(dimethyl) complex is due to its inability, through the alkyl group, to undergo McLafferty rearrangement, which can occur for alkyl chains of ethyl or greater size. *identity for this mixed ligand not confirmed.

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