ALLEN LEE GALYER

THE COORDINATION CHEMISTRY OF

SOME SULPHUR-NITROGEN LIGANDS

Submitted for the degree of Master of Science

in Chemistry at the Victoria University of Wellington

February 1969.

ABSTRACT

Some nickel(II) and copper(II) complexes of 2-(benzylthio)ethylamine have been isolated and characterised with respect to infrared and electronic spectra. With nickel(II) only the _bis_ salts were obtained and they were all paramagnetic.

An investigation of the nickel(II) and copper(II) complexes of three tetradentate ligands, each containing two sulphur and two nitrogen donor atoms, has been made. One of these, 1,9-diamino 3,7-dithianonane has been compared to the nitrogen analogue, 1,9-diamino 3,7-diazanonane.

Attempts to bridge and cyclise complexes using reactions of acetone with coordinated amino groups and halides with coordinated thiol groups are also reported.

Finally a novel S-detritylation reaction is discussed.

TABLE OF CONTENTS

INDEX OF TABLES

PART 1   A GENERAL SURVEY OF SULPHUR LIGANDS

In recent years it has become fashionable to divide the donor atoms, in metal complexes, into two groups:[1,2,3]

(a) Those atoms which are non-polarizable, or "hard". In this category are the elements which are the first members of each group in the periodic table, e.g.

N, O and F

and

(b) Those atoms which are polarizable or "soft", e.g.

S, P, As, I.

These elements are the second or subsequent elements of each group. It is found that the metal ions, or acceptors, can be classified into those which form strong complexes with type (a) ligands, and those which form strong bonds to type (b) donors. Typical type (a) metals are: Al^{3+} and Ca^{2+}, which have a noble gas electron configuration, also Co(III), Fe(III) and Ti(III) and some of type (b) are Cu(I), Hg(II), Pd(II), Pt(II) and Ag(I) which have a d^{10} electron configuration.   The metal ions, Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) are classed as "in between" (a) and (b); they can under certain conditions form strong bonds with either "hard" or "soft" donor atoms, e.g. Cu(II) has a high affinity for both nitrogen and neutral sulphur.

The sulphide ion, S^{2-}, is an example of a species that is readily polarized (high type (b) character), and also has considerable proton

basicity (typical of "hard" donors). Hence it will form strong bonds to both (a) and (b) acceptors.

The polarizability of sulphur ligands decreases in the order:[4] $S^{2-} > RS^- > R_2S$, so it is to be expected that thioethers and to a certain extent thiols, would favour "soft" acceptors. It is well known that mercury, a typical (b) type acceptor, forms very strong bonds with sulphur. In general the unidentate thioether grouping can only be complexed with the cations of very "soft" metals, and is greatly inferior to the much more basic mercaptide group.

It is found that the "borderline" metals (Ni(II), Cu(II) etc) in general will only coordinate to thioethers if there is another suitable donor in the ligand and the chelate effect operates. The coordination of a "soft" ligand to a "soft" acceptor will decrease the "soft" character of the acceptor, and so inhibit its ability to coordinate to further soft ligands. Nickel(II) will not in general complex with monodentate thioethers, but will complex with ligands also containing nitrogen (which is "hard"), especially if extra stability can be obtained from the formation of a five membered chelate ring.

e.g. Nickel(II) forms $NiL_2(ClO_4)_2$

where L is di-(2-aminoethyl)sulphide[5]

$$H_2NCH_2CH_2SCH_2CH_2NH_2$$
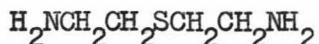
With nickel(II) the chelate effect seems to be sufficient to allow the formation of complexes with some ligands containing two thioether groups. The ligand field strength of 1,2-dialkyl di-thioethanes complexed with

nickel(II) has been found to be nearly as great as that due to ammonia bonded to nickel(II)

$$(Ni(CH_3SCH_2CH_2SCH_3)_3^{2+} \qquad Dq = 1050 \text{ cm}^{-1} \quad [6]$$

$$Ni(NH_3)_6^{2+} \qquad Dq = 1100 \text{ cm}^{-1} \quad [7]$$

The thiol (RS^-), grouping being "soft" and having relatively high proton affinity, forms very strong bonds to nickel(II). Unlike thioethers, thiols cause spin pairing in nickel(II) complexes and planar, diamagnetic products result. e.g. bis(2-aminoethane thiol)nickel(II) (I) is a stable, light green diamagnetic solid.[8] The crystal structure of the NN'-dimethyl derivative has been determined. The complex is _trans_ with the system NiS_2N_2 in one plane.[9] The compounds: N-methyl 2,2-dithiodiethylamine, $CH_3-N(CH_2CH_2SH)_2$, and 2,2-dithiodiethylsulphide $S(CH_2CH_2SH)_2$, both react with nickel to yield red crystalline solid products, soluble in halocarbon solvents. Both are diamagnetic and molecular weight determinations indicate dimeric structures.[10,11] (II). These compounds illustrate well the bridging sulphur, which is very common in complexes containing the RS^- grouping, e.g. ethylmercaptan forms a polymer with nickel(II).[4] (III) Solution equilibria studies on the system Ni(II)-ethane dithiol indicate two very stable species:[11]

$$(NiL_2)^{2-} \text{ and } (Ni_2L_3)^{2-}$$
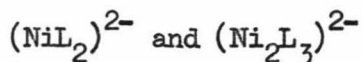
although the only solid product obtained is a black, very insoluble polymer. Jicha and Busch[12] have used this bridging ability of the mercaptide ion to prepare a series of complexes of the type. (IV). These complexes are

made by reaction of the nickel(II) and palladium(II) bis-(2-aminoethane thiol) salts (I) with the appropriate metal halides. The three metal ions are all in one plane and the mercaptide ion appears to stabilize the spin paired configuration in all the metal atoms (except for the Cu(II) complex μ_{eff} = 1.03 at room temperature).

The existence of the bis salts, used as starting materials for the last mentioned reactions, illustrates the way in which the presence of another moderately strong donor atom (nitrogen) can produce unbridged species. This can be further shown by a consideration of the nickel(II) complexes of N-alkyl and NN'-dialkyl mercapto ethylamines.[13]

$$RNHCH_2CH_2SH \qquad (Va)$$
$$R'R''NCH_2CH_2SH \qquad (Vb)$$
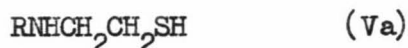
When the ligand is the N-t-butyl (R = t-butyl) or the NN'-diethyl (R' = R" = CH_3CH_2-) derivative, the nickel(II) complex is a dark insoluble powder, and unlike the products with less bulky N-substituents the N-H stretching frequency of the t-butyl adduct does not change significantly on coordination. This evidence suggests a polymeric structure with non-coordinated aminonitrogen and with bridging sulphur, similar to the ethane thiol complex, (III).

Evidence that the mercaptide ion retains its nucleophilicity when coordinated to a metal ion, first appeared in 1888. Blomstrand investigated the reaction of platinum mercaptides with alkyliodides.[14] A few papers, limited to platinum and mercury derivatives, were published on this type of reaction up to 1919.[15] These early studies were limited by the

insolubility of the reactants and products, which were very often highly polymeric. Recently Busch et al,[16,17,78] have made an extensive study of the reactions of alkyl halides with the coordinated sulphur in nickel bis-(2-aminoethane thiol) and other salts. From these investigations the following facts emerge:

1. The nucleophilicity of the coordinated thiol exceeds that of RSH, but depends on the metal atom.

2. Only the unbridged sulphurs react readily with the halide.

3. The products contain high spin, octahedral nickel, whereas the reaction complexes contain diamagnetic, square planar, nickel.

4. The metal-sulphur bond is not broken during the reaction.

5. In the case of benzylation the rate increased in an expected fashion: $PhCH_2Cl < PhCH_2Br < PhCH_2I$.

6. There is no evidence that the coordinated amino group reacted with alkyl halides.

The reactions proceed very readily if a small excess of the halide is added to a dimethylformamide suspension, or a chloroform solution, of the thiol complex, and the mixture stirred at room temperature for a few hours. Concentration of the filtrate and addition of ethanol, produces the solid complex.[16] These reactions can be represented schematically:

$$(I) \longrightarrow (VI)$$
$$(VII) \longrightarrow (VIII)$$
$$(IX) \longrightarrow (X)$$
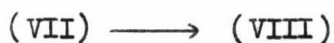
The last reaction $(IX) \longrightarrow (X)$ proceeds at a rapid rate (one hour) in chloroform. It is especially interesting, in that reaction of dihalides, able to span the end of the molecule, should enable the synthesis of a macrocyclic ring to be carried out.[18] In these cases the coordination sphere of the metal ion can be described as a slightly flexible template, which serves to hold the reactive functional groups of the ligand in the proper position to direct the steric course of the cyclisation reaction. Thompson and Busch[18] have reacted dialkyl bis-(mercapto ethylamino)nickel(II) complexes, (IX), with $\alpha\alpha$ 'dibromo-o-xylene, 1,2-dibromoethane, 1,3-dibromo and 1,3-diiodopropane. Macrocyclic rings are obtained readily with the first dihalide, a fourteen membered ring system being formed, (XI). With the other dihalides the results were not so promising, and it seems likely that 1,2-dibromoethane is too short to span the open end. Dihalopropane gives mixtures of products, presumably macrocycles and inter-molecularly linked polymers.[19] Confirmation that the dihalides can in fact link the coordinated thiol groups was obtained in the following way:

The ligand 2,2'-(o-phenylene bis-(methylthio))ethylamine (XII) was prepared[18] and reacted with nickel(II) bromide. An identical light blue solid (XIII) was obtained from the reaction: $(I) \longrightarrow (XIII)$. It can be concluded that $\alpha\alpha$'dibromo-o-xylene does react with coordinated sulphur. The complex of structure (XIII) has a magnetic moment corresponding to a triplet ground state, and is thus assumed to be octahedral. However, the macrocyclic products, (XI), have nickel in a spin paired state.

Busch has proposed an octahedral structure for the complexes of type (XI) and has cited the following experimental results to support his claim:

(a) The molecular weight determinations indicate the bromides are coordinated (in chloroform and 1,2-dichloroethane);

(b) The conductivity measurements show them to be di-univalent electrolytes in water;

(c) The electronic spectra supports an octahedral structure.

                  rare
The spin pairing (in octahedral nickel) is thought to be due to the chelate ring system constraining the nitrogens and sulphurs to a single plane, consequently shortening the metal-donor bond. This would increase the ligand field strength and spin pairing results.[19,20]

The reaction of ketones and aldehydes with primary amino groups produces Schiff base adducts (imines). Under certain conditions, in the presence of a metal ion, diamines and the carbonyl compounds can form cyclic products.[19,21,22,23] For example ethylene diamine, nickel(II) and acetone can give (XIV).[21] The reaction of ketones with 2-aminoethane thiol produces thiazolines (XV) and thiazolidines (XVI).[24,25,26]
-diketones produce (XVII) and not in general the desired Schiff base (XVIII) (up to 10% of structure (XVIII) has been isolated). However, in the presence of metal ions (Ni(II), Zn(II), Cd(II)) the products are the complexes of the Schiff base (structure (XVIII). If the compound (XVII) is heated in methanol with the metal acetate the Schiff base, complex (IX) is obtained, and it has been suggested[25] that in solution an equilibrium:

Diketone + 2-aminoethane thiol

↑↓

Schiff's base (XVIII)

↑↓

bis-thiazolidine (XVII)

is set up and the metal ion removes the Schiff's base from solution. (Solutions of thiazolidines do give positive tests for the presence of free thiol groups). A pyridine 2-aldehyde/2-aminobenzene thiol system has been studied.[27] The crystal structure of biacetyl bis-(mercaptoethylimino)nickel(II) (IX R = R' = CH_3) shows that the NiS_2N_2 system is not planar but trapezoidal (the S-Ni-N angles are $173°$ [28]). This confirms that a large ring has to be formed in the final ring closure step (IX to XI), because the system (IX) is quite strained, due largely to the highly unsaturated five membered ring.

Some interesting dealkylations of the thioether grouping have been reported.[29] The reactions include demethylation and debenzylation. The reactions can be effected by refluxing the platinum or palladium complex of the thioether in dimethylformamide for eight hours. In some cases the reaction in hot 1-butanol of a transition metal halide with a methylthioether can also cause demethylation.[30,31]

e.g. Reaction of (XIX) with nickel(II) iodide gives (XX). (The reaction was performed in a current of nitrogen and the vapours passed into alcoholic silver(I) nitrate - a pale yellow precipitate of $AgI.AgNO_3$ indicated the formation of methyliodide).[31]

This thesis examines some aspects of sulphur chemistry introduced above.

1. The synthesis and properties of the nickel(II) and copper(II) bis-chelates of S-benzyl mercaptoethylamine.

2. The synthesis and properties of some tetradentate chelate compounds containing two sulphur and two nitrogen donors and their metal complexes.

3. Attempted ring closure of some of these complexes to give complexes of macrocyclic ligands.

4. Some S-dealkylations of S and N-substituted mercaptoethylamines (catalysed by nickel(II)).

PART 2   2-(BENZYLTHIO)ETHYLAMINE (XXIV) AND ITS

METAL COMPLEXES

2.(a)   Synthesis of 2-(benzylthio)ethylamine (XXIV)

The ligand, $PhCH_2SCH_2CH_2NH_2$ (XXIV) was prepared by two methods, which gave similar yields:

(i)   The 2-aminoethane thiol hydrochloride (XXII) was obtained in 87% yield by the hydrolysis of 2-thiazoline thione (XXI), with concentrated hydrochloric acid, under reflux, for approximately 450 hours.[32]   The colourless hygroscopic salt subsequently obtained, was stored in a desiccator.   Because of the rate with which the compound absorbed water, a satisfactory infrared spectrum could not be obtained.

Melting point 67-70° (lit.[32] 70°C)

The reaction of 2-aminoethanethiol hydrochloride (XXII) with a mixture of benzyl chloride and sodium iodide, in the presence of sodium ethoxide was a modification of a procedure described in the literature.[33]

To a solution of sodium (23.4 gm, 1.02 gm-atom) in absolute ethanol (900 mls) was added 2-aminoethanethiol hydrochloride (56.7 gm, 0.50 mole). The mixture was stirred and heated to reflux temperature under a nitrogen atmosphere.   A solution of benzyl chloride (63.3 gm, 0.50 mole) and sodium iodide (74.9 gm, 0.50 mole) in absolute ethanol (350 mls) was added dropwise to the gently refluxing mixture.   When the addition was complete (ca. 1 hr), the mixture was stirred and refluxed for 14 hours under nitrogen.   The solution was allowed to cool, the precipitated inorganic salts removed by filtration, and the filtrate rotary-evaporated to a small volume.   One hundred and fifty millilitres of water was added and the amine extracted with diethylether.   The ethereal extracts (5x150 ml), were combined, washed with water and dried over anhydrous calcium sulphate for

12 hours. The ether was removed and the amine distilled through a short column –

Yield   63.6 grams (74.5%)

B.P.   130-135°C (4.0 mm)

Lit. B.P. 96-99°C (0.6 mm)[33]

(The use of the benzyl chloride/sodium iodide mixture increased the yield from 52%[33] to the 74.5% obtained above).

(ii)   A method due to Cortese[34] was used to prepare 2-bromoethylamine hydrobromide (XXIII) – 71% yield.

M.P.   173-4°C

Lit. M.P. 174-175°C[34]

% ionic Br found: 40.26% (Volhard)

$C_2H_6BrNHBr$ requires 39.50% ionic Br⁻.

The reaction of benzyl mercaptan with the halide (XXIII) in the presence of sodium ethoxide was accomplished as described by Baddiley and Thain[35] – yield 76%.

B.P.   136-142°C (4.5-5.0 mm)

Lit. B.P. 95-99°C (0.6 mm)[33]

The amine obtained from both the above methods was a colourless liquid, which rapidly absorbed carbon dioxide from the atmosphere. The compound was stored over potassium hydroxide pellets in a desiccator.

A sample of the amine dissolved in ether was cooled and hydrogen bromide gas passed in to the solution. The oil initially obtained was dissolved in hot 2-propanol and the solution filtered and cooled. The

hydrobromide salt was removed by filtration and recrystallized from 2-propanol:

$$M.P. \quad 130^{\circ}C$$

$$Lit. \ M.P. \ 129\text{-}130^{\circ}C^{33}$$

% Br found: 32.19% (Volhard)

$C_9H_{14}NSBr$ requires 32.31%.

The nuclear magnetic resonance spectrum of the amine (XXIV) was measured in $CDCl_3$ (tetramethylsilane ($\delta = 0$) standard).

TABLE 1

N.M.R. Spectrum

δ	Multiplicity	Assignment
1.27	Singlet	a
2.60	A_2B_2 pattern	b
3.63	Singlet	c
7.23	Singlet	d

$$Ph \ CH_2 \ SCH_2 \ CH_2 \ NH_2$$
$$d \quad c \quad b \quad b \quad a$$
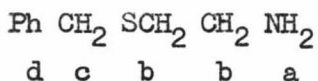
Infrared Spectrum*

The principle absorptions in the infrared region were as follows: (cm^{-1}).

Assignment			
$\bigr\}$NH	3365 s,sp;	3275 s,sp;	3170 sh
$\bigr\}$CH (aromatic)	3080 s,sp;	3060 s,sp;	3015 s,sp
$\bigr\}$CH (aliphatic)	2945 s,sp;	2915 s,sp;	2850 s,sp

Table 1 continued

Combination and overtone bands of the mono-substituted benzene ring:

		1955 w,br;	1885 w,br;	1810 w,br;	1755 w,br
ν C = C (Aromatic)		1604 s,sp;	1495 s,sp		
δ NH_2		1585 s,sp			
δ Antisym. (CH_2)		1453 s,sp			
δ CH (Aromatic)		705 s,sp;	772 s,sp		

* The following abbreviations are used:

s = strong, sp = sharp, w = weak, br = broad, sh = shoulder.

There was some difficulty assigning bands in the 1600 cm^{-1} to 1400 cm^{-1} region. The aromatic absorptions in this region are approximately 1600, 1580, 1490, 1450 cm^{-1}.[36] The amine band is approximately 1590 cm^{-1} and the antisym. CH_2 bending about 1450 cm^{-1}.[36] The aromatic absorptions were assigned to 1600 cm^{-1}, the CH_2 bending mode was placed at 1453 cm^{-1} as it is generally more intense than the aromatic band in this region. The primary amine bending vibration was assigned to 1585 cm^{-1} as this band varied over the range 1585 to 1566 cm^{-1} in the metal complexes. The absorptions at 705 and 772 cm^{-1} are characteristic of monosubstituted benzene.

2.(b) Preparation of Copper(II) and Nickel(II) Complexes of 2-(benzylthio)ethylamine

The various nickel(II) complexes were prepared in methanol solution by the following general procedure:

A methanolic solution containing 0.002 mole of the appropriate nickel(II) salt (nickel(II) chloride hexahydrate, nickel(II) nitrate hexahydrate,

nickel(II) thiocyanate hemihydrate or nickel(II) iodide), was treated with 2-(benzylthio)ethylamine (0.67 gm, 0.004 mole). The mixture was shaken for a few minutes and the solution allowed to stand overnight. The precipitated material was removed by filtration and washed with methanol, then dried in vacuo over silica gel.

The nickel(II) nitro complex was prepared by adding an excess of a concentrated aqueous solution of potassium nitrite to a methanol solution containing 0.002 moles of nickel(II) acetate tetrahydrate, 0.004 moles of the amine hydrobromide and 0.004 moles of triethylamine. The precipitate was treated in a similar manner to that described above.

The copper(II) complexes were prepared and treated in a manner analogous to the nickel salts except that solutions of copper(II) acetate monohydrate and excess sodium iodide or ammonium thiocyanate were used to prepare the iodo and thiocyanato complexes respectively.

The metal analyses were performed gravimetrically using dimethylglyoxime for nickel and salicylaldoxime for copper. The complexes were decomposed by boiling aqueous potassium peroxydisulphate or combinations of sulphuric and nitric acids. The yields, analytical results etc. are set out in Table 2.

TABLE 2

Analytical Data for copper(II) and nickel(II) complexes of 2-(benzylthio)ethylamine (XXIV)

$$M(amine)_2X_2 \ (XXV)$$

M = Ni
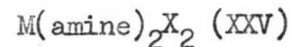
				Analysis					
				C		H		Ni	
X	Colour	Yield (%)	Solvent	Calc.	Found	Calc.	Found	Calc.	Found
Cl	Pale blue	90	MeOH	46.58	46.37	5.65	5.71	12.67	12.52
NO_3	Blue	65	DMF/iPrOH	41.79	41.79	5.07	5.23	11.35	11.50
SCN	Mauve	93	DMF/iPrOH	47.15	47.16	5.14	5.41	11.52	11.50
I	Lime	80	DMF/iPrOH	33.41	33.23	4.05	4.05	9.07	9.22
NO_2	Orange	85	MeOH	44.55	44.36	5.40	5.54	12.09	12.35

M = Cu

X	Colour	Yield (%)	Solvent	Calc.	Found	Calc.	Found	Calc.	Found
Cl	Blue-green	88	MeOH	46.10	46.06	5.59	5.70	13.55	13.37
NO_3	Blue	97	DMSO	41.41	41.08	5.02	5.07	12.17	12.30
SCN[a]	Brown	69	DMF/iPrOH	38.07	38.24	3.78	4.12	18.31	18.09
I	Dark brown	78	DMF/MeOH	33.16	32.71	4.02	4.07	9.75	9.89

[a] Calculated for Cu(amine)(SCN)$_2$

Solvent of recrystallization: MeOH = methanol
DMF = dimethylformamide
iPrOH = 2-propanol
DMSO = dimethylsulphoxide

Attempts to prepare nickel salts of the ligand (XXIV) with bidentate anions such as acetylacetonate and oxalate were unsuccessful. Addition of acetylacetone and oxalate to methanolic solutions of the amine and nickel(II) gave good yields of nickel(II) acetylacetonate and nickel(II) oxalate respectively.

A sulphito complex of nickel(II) was prepared in a manner analogous to that used for the nickel(II) nitro complex. The pale pink compound could not be recrystallised because of decomposition when heated in the solvents tried.

Analysis: Found C 5.30, 5.45%

H 1.10, 1.19%

Ni 7.61%.

These data could not be assigned to a simple structure.

As can be seen from Table 2 the only solid complexes of nickel(II) obtained were the bis products. Attempts to apply the method of continuous variations to the system were unsuccessful due to solubility problems. In order to obtain solutions of sufficient intensity in the visible region the concentrations were such that precipitation of the nickel(II) bis complex occurred almost immediately.

2.(c)   Infrared Spectra of the Metal Complexes

The spectra were determined in the region 4000 cm^{-1} to 650 cm^{-1}, on a Perkin-Elmer, model 221, infrared spectrophotometer, using nujol and hexachlorobutadiene mulls. The results are contained in Tables 3 and 4.

TABLE 3

Primary amine stretching and bending frequencies, in the range $3500\ cm^{-1}$ to $1500\ cm^{-1}$ for some nickel(II) and copper(II) complexes of 2-(benzylthio)ethylamine (XXV).

Nickel(amine)$_2$X$_2$	$\bigvee_{NH_2}$	δ_{NH_2}
X = Cl	3280 s,sp 3238 s,sp 3140 m,sp	1583 s,sp
SCN	3340 s,sp 3315 sh 3290 s,sp 3250 sh 3140 w	1575 m,br
NO$_3$	3320 s,sp 3270 m,sp 3150 w	1582 w,sh
I	3310 s,sp 3270 s,sp	1566 m,sp
NO$_2$	3280 s,sp 3230 s,sp 3145 s,sp	1585 m
Copper(amine)$_2$X$_2$		
X = Cl	3280 s,sp 3265 s,sp 3230 m,sp 3220 s,sp 3160 m,sp 3115 m,sp	1575 m,sp
SCN[a]	3330 s,sp 3275 s,sp	1576 s,sp
NO$_3$	3230 s,sp 3155 s,sp	1585 w,sp
I	3245 m,sp 3190 m,sp	1565 s,sp
2-(benzylthio)ethylamine (XXIV)	3365 s,sp 3275 s,sp 3170 sh	1585 w,sp

a   Cu(amine)(SCN)$_2$

TABLE 4

Organic C–H and C–C infrared modes for some nickel(II) and copper(II) complexes of

2-(benzylthio)ethylamine (XXV)

Nickel(amine)$_2$X$_2$	ν_{CH} aromatic	ν_{CH} aliphatic	δ_{CH} aromatic	$\nu_{C=C}$ aromatic	anti-sym. δ_{CH_2}
X = Cl	3106 w,sp 3088 m,sp 3065 m,sp 3032 m,sp 3006 w,sp 2975 m,sp 2960 m,sp	2935 m,sp 2924 s,sp 2870 m,sp	700 s,sp 771 s,sp	1604 m,sp 1494 m,sp	1448 m,sp
SCN	3080 w,sp 3055 w,sp 3025 s,sp	2965 w,sp 2955 w,sp 2930 m,sp 2877 m,sp	701 s,sp 776 s,sp	1494 s,sp	1452 s,sp
NO$_3$	3080 w,sp 3060 w,sp 3026 w,sp 2975 w,sp	2957 w,sp 2935 w,sp 2880 w,sp	700 s,sp 764 m,sp 773 m,sp	1597 m,sp 1494 w,sp	1453 w,sh
I	3100 w,sp 3075 w,sp 3055 w,sp 3025 w,sp	2970 w,sp 2950 w,sp 2925 m,sp 2874 w,sp	705 s,sp 772 s,sp	1600 w,sp 1493 m,sp	1453 s,sp
NO$_2$	3080 w,sp 3055 s,sp 3050 s,sp 3000 w,sp	2970 s,sp 2925 s,sp 2915 s,sp 2875 s,sp	695 s,sp 763 s,sp	1604 w,sp 1495 s,sp	1454 s,sp

19.

Table 4 continued

$Cu(amine)_2X_2$

X = Cl	3080 w,sp	2980 w,sp	699 s,sp	1604 m,sp	1452 m,sp
	3052 w,sp	2960 w,sp	756 s,sp	1494 m,sp	
	3027 w,sp	2950 w,sp	768 s,sp		
		2925 w,sp			
		2910 w,sp			
		2875 w,sp			
SCN[a]	3125 w,sp	2974 w,sp	696 s,sp	1605 w,sp	1454 s,sp
	3080 w,sp	2955 w,sp	770 s,sp	1496 m,sp	
	3065 w,sp	2935 w,sp			
	3028 m,sp	2920 w,sp			
		2880 w,sp			
NO_3	3080 w,sp	2930 w,sp	700 s,sp	1606 s,sp	1452 m,sp
	3065 w,sp	2910 w,sp	774 s,sp	1493 m,sp	
	3026 w,sp				
	2974 w,sp				
	2960 w,sp				
I	3110 w,sp	2950 w,sp	699 m,sp	1600 w,sp	1453 m,br
	3077 w,sp	2875 w,sp	761 m,sp	1492 w,sp	
	3055 w,sp		774 m,sp		
	3025 w,sp				
2-(benzylthio)ethylamine	3080 w,sp	2945 sh	695 s,sp	1604 s,sp	1453 s,sp
	3060 w,sp	2915 s,sp	767 s,sp	1495 s,sp	
	3025 s,sp	2850 m,sp			

a $Cu(amine)(SCN)_2$

Considerable difficulty was experienced in assigning some of the bands in the region around 3000 cm^{-1}. In this region a complex series of bands occurs, fortunately usually quite sharp, but due to variations in the resolution often difficult to assign either to aromatic or aliphatic $\int_{CH}$. Fig. (XXVI) illustrates the spectrum of bis(2-(benzylthio)ethylamine) nickel dichloride in the region of 3400 to 2800 cm^{-1}. Most of the samples had this general pattern of absorption, but poorer resolutions in some samples had the effect of turning the amine band 3140 cm^{-1} into a shoulder of the 3238 cm^{-1} amine band and merging the various C-H absorptions. A particularly complex spectrum in this region was obtained for the copper(II) dichloro complex (Fig. XXVII). The six intense amine bands are prominent and the complexity of the CH absorptions made assignment almost impossible.

The amine bands at about 3200 cm^{-1} and 1580 cm^{-1} vary from compound to compound. The decrease in frequency from that of the free ligand was in general not large. The amine stretch frequencies decrease on coordination due to a weakening of the N-H bond. It will be noted that the band positions depend on the anion and there is good evidence for the presence of hydrogen bonding between the N-H and anions such as halogens. Often the decrease due to hydrogen bonds can be shown to be greater than that due to the formation of a metal-nitrogen bond.[37] The nickel thiocyanato and copper chloro compounds show more complex amine stretching vibrations than do the others. The nickel salt is <u>cis</u> (this is concluded from the $\int$ C ≡ N vibration and the solid-state reflectance spectra) and the splitting of the two bands of highest frequency presumably is due to interactions in the crystal lattice which are different from those in the other nickel complexes. The copper complex has all three amine stretching vibrations split into doublets

giving rise to six intense bands (Fig. XXVII). Here again crystal interactions are probably responsible.

The only major difference in the bands indicated in Table 4 is the splitting of the aromatic CH deformation mode at 760 cm^{-1}, in the chloro complex of both metals and the nitrato complex of nickel as well as the iodo complex of copper. The nickel(II) sulphito complex was unusual in that the infrared spectrum showed only very broad absorptions. A large broad band occurred at 3300 cm^{-1} attributable to hydrogen bonding between the amine and anion (this envelope also contained the water bands). A broad shoulder at 1640 cm^{-1} indicated water (δOH). The two sulphite bands centred at 1130 cm^{-1} and 975 cm^{-1} were so intense that other absorptions were completely obscured in the range 1300–650 cm^{-1}.

2.(d) Infrared Spectra of the Anions (SCN, NO_3, NO_2) in Some of the Complexes

1. Thiocyanate

The following assignments were made:

Nickel νCN	2098 s,sp;	2081 sh
νC–S	802 m,sp	
Copper νCN	2077 s,sp	
νC–S	793 m,sp	

The transition metal thiocyanates can be classified into two groups (i) those which are N-bonded (isothiocyanates) and (ii) those which are S-bonded (thiocyanates). It is found that the division of the metals into "hard" and

Fig. XXVI   Infrared spectrum of bis(2-benzylthio)ethylamine)
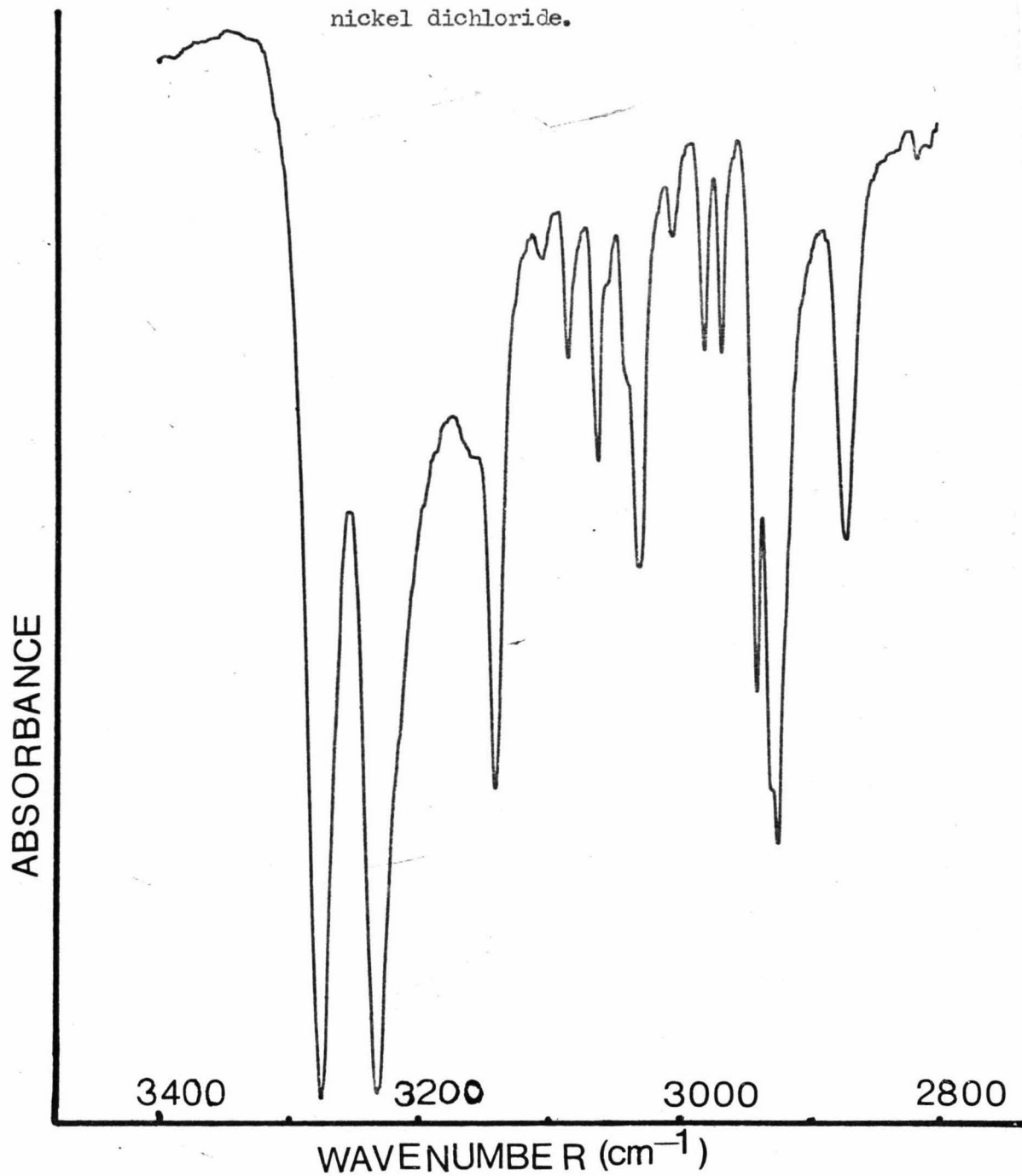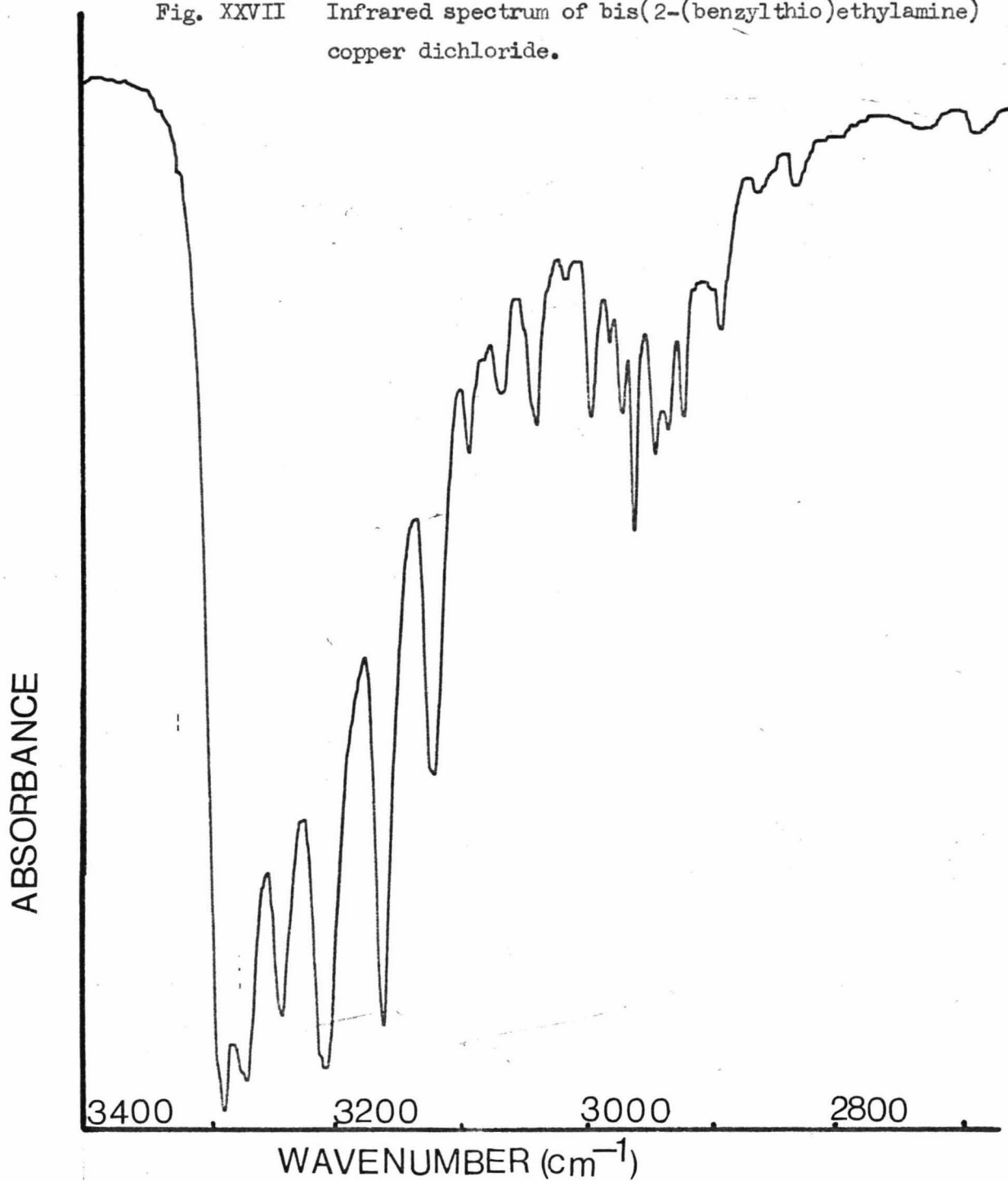nickel dichloride.

Fig. XXVII   Infrared spectrum of bis(2-(benzylthio)ethylamine) copper dichloride.

"soft" acceptors[2] is paralleled when metals are placed in (i) or (ii).
The second and third series metals are commonly S-bonded and those of the
first series generally are N-bonded to thiocyanate (except in SCN bridged
complexes, e.g. $K_2Cd(SCN)_4.2H_2O$; $Ni(NH_3)_2(SCN)_2$ [38]). If the two bonding
extremes are written as M-N=C=S and M-S-C≡N then it is expected that the
νCN and νCS frequencies should be sufficient to decide whether a complex
is S or N bonded. The CN stretching frequencies do vary with the mode of
coordination but the ranges of observed frequencies for each case overlap
and there is the added complication that factors other than the donor
atom cause variation in this vibration. The CS stretching varies
considerably, either side of the value for KNCS, viz. 749 cm^{-1}, the most
usual values being: S-bonded near 700 cm^{-1} (690-720) and N-bonded near
820 cm^{-1} (760-880).[38] As the νCS vibration is usually quite weak it is
often impossible to observe in systems containing other organic ligands
(e.g. amines, aromatics) as many skeletal and other assorted bending modes
occur in this, the "fingerprint" region. (The low frequency infrared
spectra and the visible spectra of thiocyanates will be discussed in the
appropriate sections following). On the basis of the above discussion it is
probable that both the nickel and copper complexes contain N-bonded
thiocyanate.

A splitting of the νCN band is generally regarded as being
characteristic of a cis (anion) structure. The nickel(II) thiocyanato
complex of 2-(benzylthio)ethylamine showed such splitting and hence is
presumed to be cis. The place of this complex in the spectrochemical
series supports this assignment. The copper(II) thiocyanato complex must

be **cis** as the analytical figures support the formulation $Cu(amine)(SCN)_2$, but no splitting of the νCN band is observed.

2. Nitrate

The ionic nitrate ion (D_{3h} symmetry) has three infrared active modes of vibration:

ν_2 (out of plane deformation)

ν_3 (anti-symmetric doubly degenerate stretch)

ν_4 (doubly degenerate in plane bending)

The ν_1 band (symmetric stretch) is normally infrared inactive.[39]

An example is:

$$Nien_3(NO_3)_2$$

ν_2 823 cm^{-1} m,sp

ν_3 1368 cm^{-1} s,br

ν_4 704 cm^{-1} w,sp
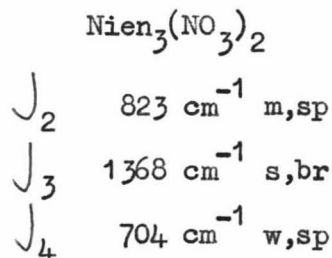
On coordination as a monodentate ligand (C_{2v} symmetry) the doubly degenerate bands ν_3 and ν_4 are split and ν_1 becomes infrared active,

e.g. $Nien_2(NO_3)_2$ [39]

ν_2 818 cm^{-1} m,sp

ν_3 1305 cm^{-1} s; 1420 cm^{-1} s

ν_4 708 cm^{-1} w,sp; 728 cm^{-1} w,sp

ν_1 -   not seen
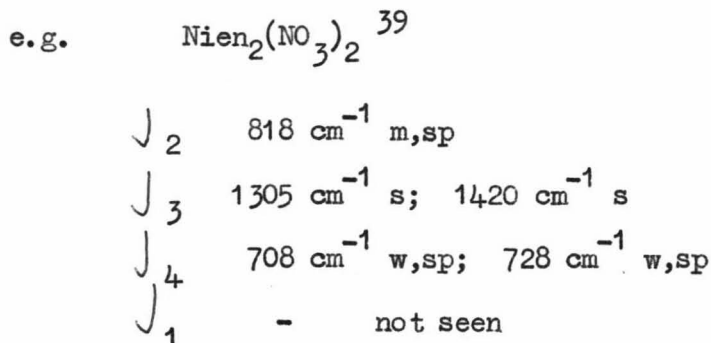
There is usually some uncertainty about the assignment of J_1, due to its weak nature and the presence of relatively strong amine bands in the region 1000–1050 cm^{-1} where J_1 is expected to lie (the band has been observed in some tetramine nitrato complexes of nickel(III).[40]) Unfortunately the nickel(II) and copper(II) nitrato complexes of 2-(benzylthio)ethylamine (XXIV) had strong absorption in the region of J_1 (1050–1000 cm^{-1}) and in the region of J_4 (700 cm^{-1}), (this strong absorption is due to amine and complicated skeletal vibrations), consequently the bands that may have been attributable to J_1 and J_4 could not be observed. However, J_2 and J_3 could be assigned with a reasonable degree of certainty and the combination and overtone peaks at approximately 1750 cm^{-1} and 2300 cm^{-1} enabled J_1 and J_4 to be estimated. The results are contained in Tables 5 and 6.

TABLE 5

Fundamental nitrate bands in the infrared region for the nickel(II) and copper(II) nitrato complexes

Complex	$M(2\text{-(benzylthio)ethylamine})_2(NO_3)_2$			J_4
	J_2	J_3		
M = Ni	814 m,sp	1282 s,br	1405 w,sp	-
M = Cu	825 m,sp	1300 s,br	1383 s,br	-
$\text{Nien}_2(NO_3)_2$ [40]	818 m,sp	1305 s	1420 s	708 w,sp
				728 w,sp

TABLE 6

Combination and overtone bands of the nickel(II) and copper(II) nitrato complexes

Complex	$\nu_1 + \nu_3$	Δ	$\Delta\nu_3$	ν_1 Calc.	$\nu_1 + \nu_4$	Δ	ν_1 Calc.	ν_4^* Calc.	Δ
Ni	2290,2430	140	123	1008,1025	1728,1750	22	-	712,734	22
Cu	2310,2410	100	83	1010,1027	1744,1773	29	-	726,755	29
$Nien_2(NO_3)_2$ [40]	2320,2455	135	115	1015,1035	1741,1762	21	1033,1034	708,728	20

* ν_4 from $(\nu_1 + \nu_4)_{obs}$ - average value of ν_1 from $(\nu_1 + \nu_3)_{obs}$

26.

A band expected at about 2000 cm^{-1} and attributable to the overtone $2\mathcal{J}_1$, could not be assigned as a similar band appeared in all the complexes studied.

The complexes show good agreement with the expected results for a _trans_ mono-dentate nitrato complex, e.g. $Nien_2(NO_3)_2$. It has not yet been possible to prepare a _bis_-nitrato salt with the nitrate groups _cis_ and monodentate. The reason for this is probably steric.

3. _Nitro_

The complex $Ni(2-(benzylthio)ethylamine)_2(NO_2)_2$ had the following absorptions in the infrared attributable to the NO_2^- anion.

$\mathcal{J}_{asym.}$	1350 cm^{-1}	s
$\mathcal{J}_{sym.}$	1310 cm^{-1}	s
δ_{ONO}	814 cm^{-1}	s,vsp

Comparing these results with the system:[41] $NiL_2(NO_2)_2$ and $NiL_2(ONO)_2$ (where L is a substituted amino pyridine)

	$\underline{\mathcal{J}_{as}}$	$\underline{\mathcal{J}_s}$	$\underline{\delta_{ONO}}$
$NaNO_2$	1328	1261	828
$NiL_2(NO_2)_2$	1334 s	1315 s	810
$NiL_2(ONO)_2$	1375 s	1180 s	817, 822

(It is often found that the nitrito, ONO, complexes are unstable, e.g. $(Co(NH_3)_5ONO)Cl_2$ slowly converts to $(Co(NH_3)_5NO_2)Cl_2$ [42]).

The different ways in which a nitro group can coordinate can be distinguished in the infrared spectra is as follows:[41]

Non-chelate		N-bonded
ν_{as}	$>$	ionic NO_2^-
ν_s		

Chelate		O-bonded
ν_{as}	$<$	ionic NO_2^-
ν_s		

Bridge		
ν_{as}	$>$	ionic NO_2^-
ν_s	$<$	ionic NO_2^-

Non-chelate		O-bonded
ν_{as}	$>$	ionic NO_2^-
ν_s	$<$	ionic NO_2^-

The last two cases can be distinguished by the fact that the stretchings in the bridged complex are higher compared to those of the monodentate nitrito complex, e.g. [37]

Bridged	1516 and 1200
Nitrito	1460 and 1050

The symmetric ONO bending at 814 cm^{-1} in $Ni(2\text{-}(benzylthio)ethylamine)_2(NO_2)_2$ indicates a _trans_ complex because a doublet is observed for _cis_ compounds.[43]

From the above discussion a _trans_ structure with N-bonded monodentate nitro anions can be deduced for the complex.

2.(e) <u>Low Frequency Infrared Spectra of Some Nickel and a Copper Complex</u>

The low frequency spectra were measured in nujol mulls, over the range 650 to 300 cm^{-1}. The results are shown in Table 7.

<u>TABLE 7</u>

Infrared spectra in the region 650 to 300 cm^{-1} for some complexes

of 2-(benzylthio)ethylamine (XXIV)

Ligand	CuL_2Cl_2	NiL_2Cl_2	$NiL_2(SCN)_2$	NiL_2I_2	$NiL_2(NO_3)_2$
			612 s,sp		
	650 s,sp	640 s,sp	645 m,sp	639 s,sp	650 w,sp
564 s,sp	563 s,sp	565 s,sp	569 s,sp	571 s,sp	571 s,sp
	514 s,sp				504 s,sp
	489 s,sp	494 s,sp			
477 s,sp	471 s,sp	478 s,sp	473 s,sp*	483 s,sp	476 s,sp
	464 w,br			465 s,sp	466 s,sp
	425 w,br			412 m,sp	417 s,sp
393 s,sp		396 m,sp			
376 w,br	376 w,br		372 s,sp	376 w,br	
351 w,br	351 w,br	357 w,br	353 s,sp	351 w,br	351 w,br
	342 w,br				
329 w,br	329 w,br	328 w,br	328 w,br	329 w,br	329 w,br

* δ NCS – see text

The only band that can be assigned to a specific vibration is the 473 cm^{-1*}.absorption in $NiL_2(SCN)_2$. This peak is attributed to δ NCS[38,44] as it was by far the most intense peak in the spectrum of this complex in the region 450-480 cm^{-1}. As it was a singlet and at 473 cm^{-1} it indicates that a metal-nitrogen bond exists between the nickel and the anion. A metal-sulphur bond would be reflected in the δ NCS mode being at

quite lower frequencies and more than one band would be expected.

Metal-sulphur stretching frequencies are in the range 480-210 cm^{-1} [45] but are often difficult to detect as they tend to be weak and quite broad. In some cases, however, definite assignments can be made. The complexes $PdCl_2(RSCH_2CH_2SR)$ R = CH_3, Ph have been investigated:[46]

When R = CH_3 ν Pd-S is 338.5 cm^{-1}

When R = Ph[46] ν Pd-S is 331 cm^{-1} and 312 cm^{-1}.

In the series $MX_2(PhSCH_2CH_2CH_2SPh)$ M = Pd,Pt, X = Cl,Br.
The following assignments were made[47] for ν_{M-S}

$PdCl_2$	323 cm^{-1} s	308 cm^{-1} s
$PdBr_2$		316 cm^{-2} s
$PtCl_2$	350 cm^{-1} s	329 cm^{-1} s
$PtBr_2$	349 cm^{-1}	324 cm^{-1} w

In the case of ethylene diamine complexes of metals the ν_{M-N} bands are in the range 590-506 (cm^{-1}),[45] but generally chelate compounds have such strong ring modes that are coupled to other skeletal vibrations that to assign a particular peak to a particular vibration is meaningless. Even normal coordinate analysis cannot, in some cases, resolve spectra. For example, Nakamoto[48] using 75 internal coordinates has carried out a normal coordinate analysis on the complex $Fe(CH_3N=CHCH=NCH_3)_3$. The calculations showed that the coupling between the vibrational modes was very strong and hence no one band could be assigned to ν Fe-N. The bands at 756, 742, 655, 631 cm^{-1} are due to ν Fe-N + ν N-CH_3 and most of the other peaks are ascribed to sums of two modes.

It is apparent that simple interpretations of lower frequency spectra are not readily obtained and the spectra obtained from the amino-sulphide complexes considered here are no exception.

2.(f)   Electronic Spectra of the Nickel(II) Complexes

The solid state electronic spectral data of the nickel(II) complexes of 2-(benzylthio)ethylamine (XXV) are contained in Table 8 and some are illustrated in Fig. XXVIII.

TABLE 8

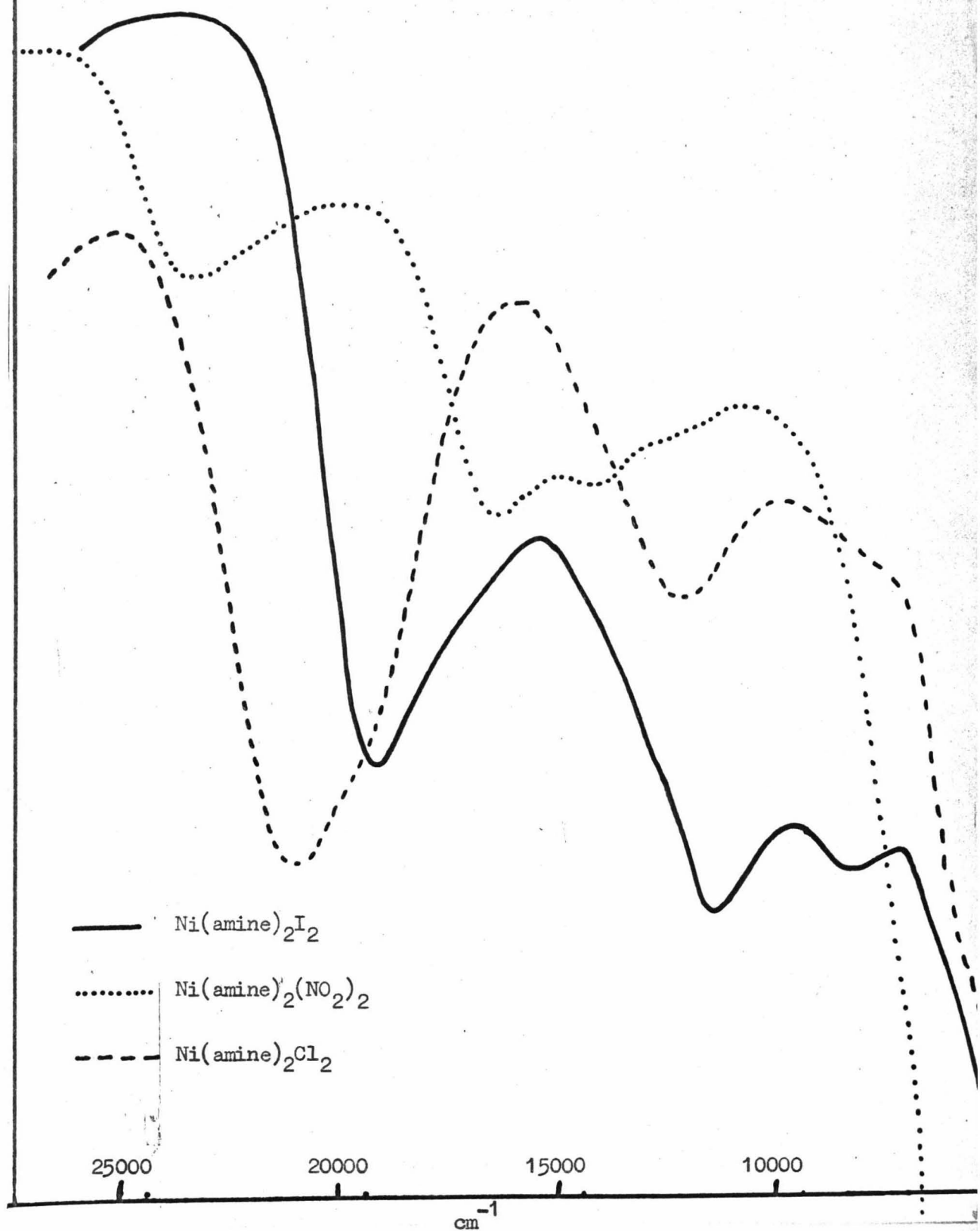Electronic spectra of some nickel(II) complexes of 2-(benzylthio) ethylamine (frequencies in cm^{-1})

	ν_3	ν_2	ν_1	10Dq
Ni(amine)$_2$Cl$_2$	25700	16500	10300	10300
(NO$_3$)$_2$	26900	16700	10900 7900	9400
(SCN)$_2$	28300	18000	8900	8900
I$_2$	24500	15900	9800 7400	8600
(NO$_2$)$_2$	26700	20400	15700 11600	11600

The spectra were all obtained on a Unicam SP700 spectrophotometer with a diffuse reflectance accessory (magnesium carbonate reference). The 10Dq values were the average of the ν_1 peaks when these were a pair as in the nitrato and iodo complexes.

The complexes were very insoluble in most solvents and decomposed in water when it was heated to dissolve them. A solution prepared by

Fig. XXVIII   Electronic spectra of some nickel(II)
                complexes of 2-(benzylthio)ethylamine

—————— Ni(amine)$_2$I$_2$

············ Ni(amine)$_2$(NO$_2$)$_2$

— — — — Ni(amine)$_2$Cl$_2$

25000   20000   15000   10000

cm^{-1}

heating the complex in dimethyl-formamide was not considered to be a satisfactory solution of the solid complex and solution spectra were not run. Busch et al[16] have measured the electronic spectra of the nickel(II) bromo and iodo complexes of this ligand in dimethyl-formamide, dimethyl sulphoxide and in chloroform. Substantial solvent dependence was found, the ligand field strength parameter (Dq) increasing, for the bromo complex, from 860 cm^{-1} in chloroform to 915 cm^{-1} (DMSO) to 930 cm^{-1} (DMF), indicating a progressive increase in the ligand field strength as the solvent becomes a better ligand. Busch used the value 860 cm^{-1} as the true value of the ligand field made up of two primary amines, two thioethers and two bromides. It is best to be wary of Dq values obtained from solution spectra, as even in solvents such as chloroform, which are assumed to be non-coordinating, ligand exchange can occur, e.g. the infrared spectrum of a chloroform solution of $Mn(CO)_3py_2NO_3$ indicates a steadily growing band at 1362 cm^{-1}, assigned to ionic nitrate and the disappearance of the covalent bands of the nitrate ion.[49]

The spectrochemical series found in most series of inorganic complexes is:[50,51]

$$I^- < {}^*SCN^- < Cl^- < {}^*NO_3^- < NO_2^{-*} < {}^*NCS^- < {}^*NO_2^-$$
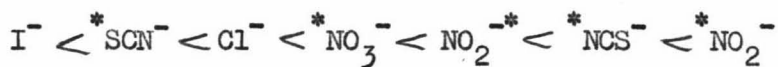
* denotes the donor atom.

For the nickel(II) complexes of 2-(benzylthio)ethylamine the Dq values indicate a series:

$$I^- < SCN^{*-} < {}^*NO_3^- < Cl^- < {}^*NO_2^-$$
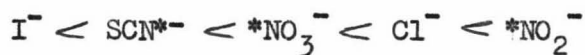
It is observed that the thiocyanate is out of place compared to the other anions and the nitrate and chloride anions have their relative positions reversed. For conclusions from the spectrochemical series to be valid the series of complexes must have known structural similarities. The infrared data indicate the thiocyanate anions are _cis_ and N-bonded to the nickel(II) ion. This is a possible explanation for the anomalous position of the thiocyanate in the spectrochemical series for the complexes if it is assumed that the others are _trans_ (anion). The infrared spectra indicates that the nitrate anions are covalently bonded to the nickel(II) and this usually means that the anions are _trans_. As nitrate and chloride are close to one another in the spectrochemical series the reversal of positions is probably not significant.

A regularly octahedral nickel(II) complex will have an electronic absorption spectrum consisting of just three bands,

	$\smallint_1$	$\smallint_2$	$\smallint_3$
e.g. $Ni(H_2O)_6^{2+}$	9000 cm^{-1}	14000 cm^{-1}	25000 cm^{-1}
$Nien_3^{2+}$	11000 cm^{-1}	18500 cm^{-1}	30000 cm^{-1}

and these bands can be assigned to a specific d-d transition by referring to some of the level energy diagrams that have been constructed for a d^8 system.[7,52,53] The accepted assignments are:

$$\smallint_1 \quad {}^3A_{2g}(F) - {}^3T_{2g}(F)$$
$$\smallint_2 \quad {}^3A_{2g}(F) - {}^3T_{1g}(F)$$
$$\smallint_3 \quad {}^3A_{2g}(F) - {}^3T_{1g}(P)$$

The $\jmath_2$ band in $Ni(H_2O)_6^{2+}$ is split due to a spin-orbit coupling, which mixes the $^3T_{1g}(F)$ and $^1E_g(D)$ states which are very close in energy in this species. In complexes such as $Nien_3^{2+}$ these two levels are sufficiently far apart so as to make this mixing insignificant. The band $\jmath_1$ ($^3A_{2g}(F) - {}^3T_{2g}(F)$) is given the value 10Dq and is used as a measure of the strength of the ligand field which surrounds the nickel ion. The positions of the bands can be predicted from an energy level diagram and any splitting that is small in magnitude, is assigned to the mixing of levels by spin-orbit coupling. Energy differences of the bands which are larger in magnitude, i.e. greater than about 1000 cm^{-1}, can often be associated with spin forbidden transitions.[7]

A great many complexes do not contain the metal ion surrounded by a regular octahedron of donor atoms and in these cases if the deviations from regularity are large, the energy level diagrams (Orgel, Liehr-Ballhausen, Tanabe-Sugano) fail to correlate the peak positions and the splittings which may occur. Since the ligand 2-(benzylthio)ethylamine has two different donors (N and S) and these are unsymmetrically substituted ($PhCH_2S$ and NH_2), the symmetry of the in-plane ligand field may either be cis (C_{2v}) or trans (D_{2h}). Because of the steric requirements of the benzyl groups D_{2h} symmetry is most likely. In passing from octahedral to lower symmetry classes the energy levels pass into other levels and in some cases the degeneracy may be lifted[54]. If the bands in the electronic spectra of complexes with pseudo-octahedral symmetry, are split to an extent that spin-orbit coupling is not the sole cause, then the band assignments must come from energy level diagrams calculated for lower symmetry. It is observed that in tetragonally distorted complexes the band $\jmath_1$ is frequently

split and that J_3 and J_4 remain unsplit because transitions observed in solid state spectra are generally rather broad. If the energy difference between two levels, in an excited state, is less than about 1500 cm^{-1} transitions are unlikely to be resolved.[55] The nickel(II) nitrato and iodo complexes have four bands and in D_{2h} symmetry the following assignments are made:[45]

$$J_{1a} \quad {}^3B_{1g} \ (F) - {}^3B_{2g} \ (F)$$

$$J_{1b} \quad {}^3B_{1g} \ (F) - {}^3B_{3g} \ (F)$$

$$J_2 \quad {}^3B_{1g} \ (F) - {}^3B_{2g} \ (F), \ {}^3B_{2g} \ (F)$$

$$J_3 \quad {}^3B_{1g} \ (F) - {}^3B_{2g} \ (P), \ {}^3B_{2g} \ (P)$$

Some estimates of the tetragonal distortion present in the complexes are contained in Appendix 1.

2.(g) <u>Magnetic Susceptibilities of the Nickel(II) Complexes</u>

The magnetic susceptibilities were measured by the Faraday method, using a six inch Varian electromagnet at a field strength of 16000 gauss, and a Cahn electrobalance. The apparatus was calibrated with $Hg(Co(CNS)_4)$[56] and $(Ni(en)_3)S_2O_3$.[57]

TABLE 9

Magnetic data for the nickel(II) complexes of 2-(benzylthio)

ethylamine (XXV)

	$10^3\chi_m$	$10^3\chi_D$	$10^3\chi_{TIP}$	$10^3\chi_m^{corr}$	T^oK	μ_{eff}
Ni(amine)$_2$Cl$_2$	3.88	0.29	0.20	3.97	298.2	3.07$\pm$0.10
(NO$_3$)$_2$	4.28	0.28	0.22	4.34	298.2	3.22$\pm$0.10
(SCN)$_2$	4.07	0.31	0.23	4.15	298.2	3.15$\pm$0.10
I$_2$	4.08	0.34	0.24	4.18	298.2	3.16$\pm$0.10
(NO$_2$)$_2$	3.03	0.26	0.18	3.11	298.2	2.73$\pm$0.10
~~(SO$_3$)$_2$~~	~~3.34~~	~~0.50~~	~~0.23~~	~~4.61~~	~~298.2~~	~~3.33$\pm$0.10~~

$$\chi_m = \chi_g \times \text{mol.wt.}$$

χ_D - from Pascal's Constants[58]

$$\chi_{TIP} = \frac{8N\beta^2}{10Dq} \quad [59]$$

$$\chi_m^{corr} = \chi_m - \chi_D - \chi_{TIP}$$

$$\mu_{eff} = 2.828 \ (\chi_m^{corr}T)^{\frac{1}{2}} \ \text{B.M.}$$

When a free nickel ion is incorporated in a complex of octahedral symmetry the ligand field lifts the degeneracy of the $^3F_4$ term to give a non-degenerate $^3A_{2g}$ lowest term. In the absence of orbital angular momentum in this ground term the magnetic moment is given by:

$$\mu_{eff}^{\text{spin only}} = (4S(S+1)^{\frac{1}{2}}\beta$$

Where S is the spin quantum number for the term and β is the Bohr magneton.

Above this $^3A_{2g}$ level lies the $^3T_{2g}$ term and due to spin-orbit coupling between the two, the quenching of orbital momentum by the ligand field is not complete. The magnetic susceptibility of the complex will be modified by a term due to spin-orbit coupling which will contain the spin-orbit coupling constant (λ) and the difference in energy between the two levels (10Dq). Using the wave functions for the $^3A_{2g}$ and the $^3T_{2g}$ terms and the operator for spin-orbit coupling, it is possible to show –

$$\mu_{eff} = (1 - \frac{4}{10Dq})\,\mu_{eff}^{spin\ only}[59]$$

There is also a second order Zeeman effect between the ground $(^3A_{2g})$ and higher energy states. It is this effect which is responsible for any temperature independent paramagnetism associated with the complex.[60] The contribution to the susceptibility is small and the expression for its estimation is:

$$\chi_{TIP} = \frac{8N\beta^2}{10Dq} \qquad N\beta^2 = 0.261\ cm^{-1}\ [59]$$

(As can be seen from Table 9 the TIP term is only slightly smaller than the diamagnetic correction and thus almost cancels it out).

There is an effective reduction of the orbital angular momentum of a metal ion consequent upon the delocalization of electrons out of the t_{2g} orbitals of the ion onto the ligand atoms. The effect of this t_{2g} delocalization is to bring the magnetic moment closer to the spin-only value, since it corresponds to an additional quenching of orbital angular momentum. For $^3A_{2g}$ terms the effect of the delocalization is to reduce the value of λ by a factor k and to introduce this factor k into the TIP term.

The total susceptibility for a $^3A_{2g}$ term is now:

$$\mu_{eff} = \mu_{eff}^{spin\ only}\ (1 - \frac{4k\lambda_o}{10Dq}) + \frac{8k^2N\beta^2}{10Dq} \qquad \text{Eqn. 3}$$

where λ_o is the spin-orbit coupling constant for the free nickel(II) ion.

Departures from cubic symmetry introduce ligand-field components of low symmetry which tend to lift the degeneracy of T terms. These components will thus markedly affect the magnetic properties of T terms. The nickel(II) triplet ground state being $^3A_{2g}$ will be unaffected.

Using equation 3 it is possible to estimate k, the t_{2g} electron delocalization parameter.

TABLE 10

Calculation of k, the t_{2g} electron delocalization parameter for some nickel(II) chelates of 2-(benzylthio)ethylamine

$10^3\chi_m^{corr}$	$10Dq\ (cm^{-1})$	k(eqn. 3)	Complex
4.17	10,300	0.91	$Ni(amine)_2Cl_2$
4.56	9,400	1.00	$(NO_3)_2$
4.38	8,900	0.95	$(SCN)_2$
4.42	8,600	0.95	I_2
3.29	11,600	-	$(NO_2)_2$
4.84	9,200	1.15	$(SO_3)_2$

$10^3\chi_m^{corr}$ does not include the TIP term as it is in eqn. 3.

10Dq from Table 8.

Eqn. 3 was used in the form:

$$\chi_m^{corr} = \chi_m^{spin\ only}\ (1 - \frac{8k^2\lambda_o}{10Dq}) + \frac{8k^2N\beta^2}{10Dq}$$

where $\chi_m^{spin\ only} = 3.333 \times 10^{-3}$ c.g.s.

$\lambda_o \qquad = -315\ cm^{-1}$

$N\beta^2 \qquad = 0.261\ cm^{-1}$

The accuracy of the measurement of magnetic susceptibility, and the difficulties of correcting accurately for the diamagnetic components, do not allow the evaluation χ_m to better than about $\pm 25 \times 10^{-6}$ c.g.s./mole and if there are large numbers of diamagnetic atoms in the ligand groups, the uncertainty is even larger. Assuming an error of ± 25 c.g.s. in the χ_m values and an uncertainty in 10Dq of 100 cm^{-1}, the uncertainty in k is found to be ± 0.15. The results of Table 10 indicate, therefore, that there is little t_{2g} electron delocalization.

The abnormal magnetic moment of the nickel(II) nitro complex is difficult to explain as all the other complexes have moments expected from paramagnetic nickel(II) complexes (2.8 to 3.5 B.M.). The compound is orange and does not change colour on cooling in liquid air, nor does it change colour before it decomposes when heated, so it is unlikely that the ligand field is near the "cross-over" point for paramagnetism to diamagnetism. The peak at 20,400 cm^{-1} is more intense than the peak at 15,700 cm^{-1} and could thus be due to a small amount of diamagnetic impurity. Any diamagnetic impurity would affect the analysis of the product but the solid was readily

recrystallized from methanol to give an analytically pure compound. The best way to determine if the substance was magnetically homogeneous would be to measure the susceptibility at different temperatures and see if the data fitted a Curie-Weiss Law.

2.(h) Electronic Spectra of the Copper(II) Complexes (XXV)

Copper(II) has the electronic configuration $(argon)(3d)^9$. The structure of a copper(II) complex will be a distorted octahedron, (Jahn-Teller effect), which in the limit goes to a square planar configuration. In an octahedral ligand field the ^2D ground state for the free ion is split into a ^2E_g and $^2T_{2g}$ level and in a ligand field of D_{2h} symmetry, as is presumed for these complexes, the degeneracy is lifted further: Fig. (XXIX)
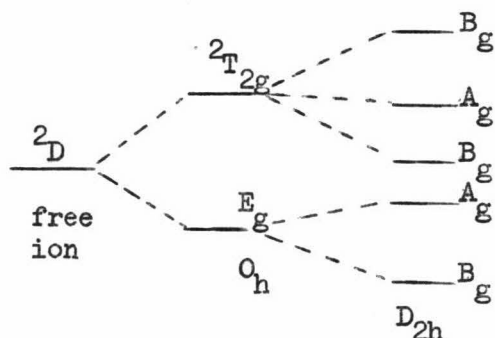
The actual order of the energy levels in D_{2h} symmetry has not been determined with any degree of certainty. The peak envelopes contain a number of transitions and the resolution even at low temperatures is often poor.

TABLE 11

Electronic Spectral Data for Some Copper(II) Complexes of

2-(benzylthio)ethylamine   (XXIV)

(all frequencies cm^{-1})

Complex	Charge transfer to:		
$Cu(amine)_2Cl_2$	26800	14300	11900 sh
$Cu(amine)_2(NO_3)_2$	26000	17300	
$Cu(amine)(SCN)_2$	7000		
$Cu(amine)_2I_2$	7000		

(The spectra were obtained in a manner similar to that discussed in sect. 2.(f)).

Table 11 indicates split bands for the chloro complex, the magnitude of this splitting being 2400 cm^{-1}. The spin-orbit coupling constant for the Cu(II) ion is -829 cm^{-1} and so the maximum splitting that could be attributed to spin-orbit coupling alone is 1244 cm^{-1}.[61] It can be concluded that this complex is structurally quite distorted, a conclusion in accord with the observations on the analogous nickel(II) complexes. Because of the asymmetry of the complexes and the uncertainty in the relative energies of the electronic levels, only qualitative deductions from Table 11 may be made.

The electronic transitions of the copper(II) thiocyanato and iodo complexes are entirely masked by change-transfer bands. The greater the "oxidising" power of the metal ion and the greater the "reducing" power

of the ligand group, the lower the energy at which charge-transfer bands appear.[59] Copper(II) is quite readily reduced and iodide is very easily oxidised and these two coupled with an organic residue containing an extensive π orbital system (benzene ring) and polarizable sulphur, leads to a complex quite well equipped for delocalization of electrons over the molecular orbitals of the system, with electrons being transferred to the copper ion.

Thiocyanato complexes always have a band at 30,000 to 37,000 cm^{-1} [51] and these transitions are probably due to π-electron transfers from the S-C≡N to the metal ion. With the more extensive π bonding present in these complexes (XXV) with copper, it is not really surprising that the change transfer bands are shifted well into the visible region.

2.(i) Magnetic Properties of the Copper(II) Complexes (XXV)

TABLE 12

Magnetic susceptibilities of some copper(II) chelates of
2-(benzylthio)ethylamine

Complex	$10^3 \chi_m$	$10^3 \chi_D$	$10^3 \chi_m$ corr.	$T^o K$	μ_{eff}
Cu(amine)$_2$Cl$_2$	1.09	0.29	1.38	298.2	1.81$\pm$0.10
Cu(amine)$_2$(NO$_3$)$_2$	1.50	0.28	1.78	298.2	2.06$\pm$0.10
Cu(amine)(SCN)$_2$	1.11	0.31	1.42	298.2	1.83$\pm$0.10
Cu(amine)$_2$I$_2$	1.29	0.34	1.63	298.2	1.97-0.10

(The susceptibilities were determined in a similar manner to the nickel(II) compounds; Table 9).

Because of the difficulties associated with the determination of 10Dq for the copper complexes no meaningful estimate of the TIP and t_{2g} electron delocalization could be made.

Table 12 indicates that the moments are all normal for copper(II) complexes (usual range 1.80 to 2.50 B.M.) i.e., about 1.9 B.M. at room temperature, an expected result as 10Dq will be in the range 11,000 to 13,000 cm^{-1}, and the spin-orbit coupling constant will be slightly below the free-ion value of -850 cm^{-1}. The results of Table 12 are in accord with the proposition that the magnetic moments of copper(II) complexes should not vary to any great extent with stereochemistry.

2.(j) X-ray Diffraction Patterns for the Nickel(II) Complexes of 2-(benzylthio)ethylamine (XXV)

The patterns were obtained on a Phillips X-ray diffractometer using Cu $K\alpha$ radiation.

The results obtained were largely negative as the patterns could not be matched between any pair of complexes.

TABLE 13

X-ray diffraction data for some nickel(II) complexes of 2-(benzylthio)
ethylamine (XXIV)

(d spacings in Å are quoted, the figures in parenthesis being the relative
peak heights).

Cl_2		$(NO_3)_2$		$(SCN)_2$		I_2		$(NO_2)_2$	
14.50	(25)	14.85	(1)	10.28	(4)	12.36	(3)	11.8	(25)
7.25	(1)	12.35	(14)	7.59	(7)	9.65	(2)	7.43	(3)
6.075	(1)	7.53	(10)	7.24	(5)	9.31	(1)	6.10	(3)
5.98	(1)	6.19	(7)	6.05	(3)	8.075	(2)	5.75	(7)
5.636	(1)	5.735	(1)	5.41	(1)	7.275	(3)	5.44	(1)
5.438	(1)	5.645	(1)	4.98	(2)	6.150	(1)	5.17	(2)
5.160	(1)	5.356	(3)	4.76	(3)	4.795	(1)	4.85	(1)
4.888	(1)	4.385	(1)	4.62	(1)	4.418	(1)	4.59	(2)
4.312	(1)	4.230	(1)	4.24	(2)	3.986	(2)	4.42	(3)
4.059	(2)	4.115	(3)	4.136	(2)	3.770	(1)	3.825	(3)
3.952	(2)	3.900	(4)	3.757	(3)	3.625	(2)	3.635	(1)
3.604	(2)	3.770	(3)	3.602	(1)	3.486	(1)	3.535	(2)
3.353	(1)	3.620	(1)	3.415	(1)	3.357	(1)	3.403	(2)
3.115	(1)	3.351	(1)	3.349	(5)	2.836	(1)	3.364	(1)
2.925	(2)	3.243	(5)	3.177	(1)	2.604	(1)	3.267	(2)
2.707	(1)	3.105	(2)	3.038	(1)	2.496	(1)	2.898	(5)
2.6595	(1)	2.637	(2)	2.955	(1)			2.768	(2)
22.526	(1)	2.507	(4)	2.904	(2)			2.571	(2)
2.478	(2)	2.464	(1)	2.806	(1)			2.455	(1)
2.410	(1)	2.222	(1)	2.702	(1)			2.407	(8)
2.3095	(1)	2.139	(1)					2.344	(1)
		2.103	(1)					2.304	(2)
								2.236	(2)
								2.126	(1)
								2.043	(1)

PART 3   SOME SULPHUR-NITROGEN TETRADENTATE CHELATES

OF COPPER(II) AND NICKEL(II)

3-1. Complexes Derived from 1,9-diamino 3,7-dithianonane (XXX)

$$H_2NCH_2CH_2SCH_2CH_2CH_2SCH_2CH_2NH_2 \text{ "A"}$$
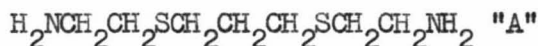
3-1(a) Preparation of the ligand "A"

To a solution of sodium (25.4 grams, 1.1 gm-atom) in ethanol (400 ml) was added, with stirring under nitrogen, 2-aminoethanethiol hydrochloride (67.5 grams, 0.5 moles). The mixture was refluxed whilst a solution of 1,3-dibromo propane (50 grams, 0.25 moles) and sodium iodide (75 grams, 0.5 moles) in absolute alcohol (300 mls) was added dropwise. When the addition was complete (ca. 3 hours) the mixture was refluxed with stirring under nitrogen for twenty hours. After cooling and filtration the solution was rotary-evaporated. The oil obtained was treated with 2 molar aqueous sodium hydroxide (50 mls) and extracted continuously into ether for four days. The ether and amine layers were separated and the ethereal solution of the amine evaporated and the oil obtained added to the separated amine. The amine was dried with potassium hydroxide pellets and distilled.

Yield 36.1 grams (73%)

B.P. 168-175°C 1.0 mm.

Lit. B.P. 147°C at 0.7 mm.[62]

The product solidified on standing overnight in a refrigerator but slowly melted at room temperature.

Infrared (cm^{-1})			
ν_{NH}	3360 s,sp	3275 s,sp
ν_{CH}	2915 s	2850 s,sp
δ_{NH}	1590 s,br	

3.1(b) Metal complexes of "A" (XXX)

TABLE 14

Complexes of 1,9 diamino 3,7-dithianonane "A"

Complex	Colour	Analysis					
		C		H		M	
		calc.	found	calc.	found	calc.	found
$NiACl_2$	blue-green	25.95	25.90	5.60	5.78	18.12	17.88
$NiA(SCN)_2 \cdot \frac{1}{2}DMF$	mauve	30.51	30.17	5.21	5.21	14.91	14.93
$CuACl_2$	dark-green	25.57	25.14	5.52	5.74	19.32	19.20

All the complexes were prepared, in almost quantitative yield, by mixing equimolar amounts of the appropriate metal salt and amine ("A") in methanolic solution. The products precipitated immediately and were removed by filtration and dried over P_2O_5 with continuous pumping. Attempts to prepare the following complexes resulted in oils or gums:

$NiA(NO_3)_2$; $NiAI_2$; $CuA(NO_3)_2$; $CuA(SCN)_2$; $CuAI_2$.
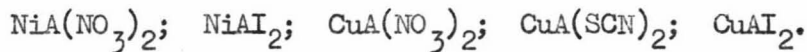
The nickel(II) chloro complex of A was insoluble in all solvents tested, hot or cold. It decomposed when heated in water but could be boiled in dimethylformamide or dimethyl sulphoxide without any apparent effect. The complex was carefully washed with hot DMF before analysis.

The copper(II) chloro complex precipitated from a royal blue solution (λ_{max} 16,600 cm^{-1}, 602 mμ) and the green anhydrous product was soluble only in water, in which it slowly decomposed. Heating in all solvents caused decomposition. The complex was washed with methanol before analysis.

The nickel(II) thiocyanato complex was recrystallized from dimethylformamide/n-butanol. The infrared spectrum showed a fairly strong peak at 1655 cm^{-1} which did not disappear after the solid was pumped overnight over P_2O_5. An examination of the literature revealed the following peak positions for dimethylformamide O-bonded to a metal ion:

TABLE 15

C = O stretching frequencies in some transition metal complexes containing dimethylformamide

Complex	$\nu_{C=O}$	Ref.
$WO_2Cl_2 \cdot 2DMF$	1640 s, 1655 br	63
$MoO_2Cl_2 \cdot 2DMF$	1653 s	64
$[Mo_6Cl_8(DMF)_6](ClO_4)_2$	1640 s	65
$Mo_6Cl_{12}(DMF)_2$	1650 s	65
$Mo_6Cl_8(DMF)_2(CH_3SO_3)_4$	1650 s	65
DMF	1670 s	

A study of the complex $[Ni(DMF)_6](ClO_4)_2$ in solution indicates the value of the ligand field parameter 10Dq to be 8400 cm^{-1} [66], i.e. DMF is quite a strong ligand. The carbonyl stretching frequency in $Ni(A)(SCN)_2 \cdot \frac{1}{2}DMF$ is 1655 cm^{-1} a shift of 15 cm^{-1} from the C=O stretch in pure DMF. Decreases of 10 to 35 cm^{-1} are generally observed in O-bonded DMF complexes.[63]

3.1(c) Spectra and structure of some complexes of "A"

3.1(c)(i) Infrared spectra

TABLE 16

(all values cm^{-1})

	ν_{NH}	ν_{CH}	δ_{NH}
$Ni(A)(SCN)_2\frac{1}{3}DMF$	3290 s,sp 3225 s,sp 3140 s,sp	2960 sh 2945 s,sp 2910 s,sp 2865 s,sp	1585 m
$Ni(A)Cl_2$	3280 s,sp 3225 s,sp 3155 s,sp	2980 w,sp 2965 m,sp 2940 w,sp 2924 s,sp 2910 s,sp 2874 m,sp	1583 m
$Cu(A)Cl_2$	3260 s,sp 3215 s,sp 3135 s,sp	2965 w,sp 2950 m,sp 2920 s,sp 2900 s,sp 2865 m,sp	1586 m
A	3360 s,sp 3275 s,sp	2915 s 2850 s,sp	1590 s,br

The spectra of all three complexes are very similar, the amine stretching frequencies are decreased by about 100 cm^{-1} and the amine bending band is shifted 5 to 7 cm^{-1}.

In the thiocyanato complex the $\nu_{C\equiv N}$ band was prominent at 2115 cm^{-1} and the band showed no evidence of splitting. Complexes containing cis thiocyanates frequently have a split $\nu_{C\equiv N}$ absorption band so it is likely that $NiA(SCN)_2\frac{1}{3}DMF$ has a trans (anion) structure. (The ν_{C-S} absorption could not be detected). In the fingerprint region all the complexes showed

rather complex but quite similar absorptions so it is reasonable to assume that they all have the trans (anion) configuration.

3.1(c)(ii) Electronic spectra

TABLE 17

Solid-state reflectance spectra of the complexes of (XXX)
(cm^{-1})

$NiA(SCN)_2\frac{1}{3}DMF$	29000	18700	11500
$NiACl_2$	26000	16200	9800
$CuACl_2$	23000*	14600	12900 sh

* an intense charge-transfer band extends to 23000 cm^{-1}.

For the two nickel complexes assuming they have the same configuration (anions axial), the spectrochemical series is SCN> Cl. This implies the thiocyanate is N-bonded to the nickel. The absence of splitting could be an indication that tetragonal distortion is not pronounced in these nickel compounds. The band assignments in the nickel(II) spectra are as in section 2.(f).

The electronic spectrum of the copper (A) dichloride complex is typical of a pseudo-octahedral copper(II) complex. The pronounced shoulder is probably a consequence of the distortion always present in six coordinate copper(II) complexes. To determine whether the copper(II) chloride complex in solution was 1:1, or some other ratio, the method of Continuous Variations[67] was applied to the system. Solutions 0.0066 molar

(aqueous methanol) in ligand and copper(II) chloride were used and the absorption at 580 mμ, 600 mμ and 625 mμ measured on a Uvispek spectrophotometer.

The Beer-Lambert law can be expressed

$$\log \frac{I_o}{I} = D = \mathcal{E}\,c\,t$$

For a solution containing ligand (L), metal ion (M) and complex (ML$_n$)

$$D_{measured} = (\mathcal{E}_M\,c_M + \mathcal{E}_L\,c_L + \mathcal{E}_{ML_n}\,c_{ML_n})t$$

and if there had been no reaction

$$D_{theoretical} = (\mathcal{E}_M\,m(1-x) + \mathcal{E}_L m\,x)t$$

where m is the molar concentration of M and L and x is the mole fraction of ligand. It follows that:

$$Y = D_{meas.} - D_{theor.} = D_{meas.} - (1-x)D_M$$

where $D_M = \mathcal{E}_M m$ (i.e. optical density of M) and it is assumed $\mathcal{E}_L = 0$ and t = 1 cm. A plot of Y vs. x will have a maximum at $x = \frac{1}{2}n$.

The data are contained in Appendix 2 and the curve for 580 mμ is shown in Fig. (XXXI). It indicates that copper(II) chloride and "A" form a 1:1 complex in aqueous methanol.

The behaviour of the system at high ligand concentrations appears to suggest the formation of another complex species with an absorption maximum outside the range 580 to 625 mμ. Solutions 5 to 10, i.e. mole fraction of ligand 0.5 to 1, were examined over the range 333 mμ to 2500 mμ

Fig. XXXI. Job plot for copper(II) chloride and ligand A (XXX)

$\lambda = 580\,m\mu$

Optical Density

Mole Fraction of Ligand
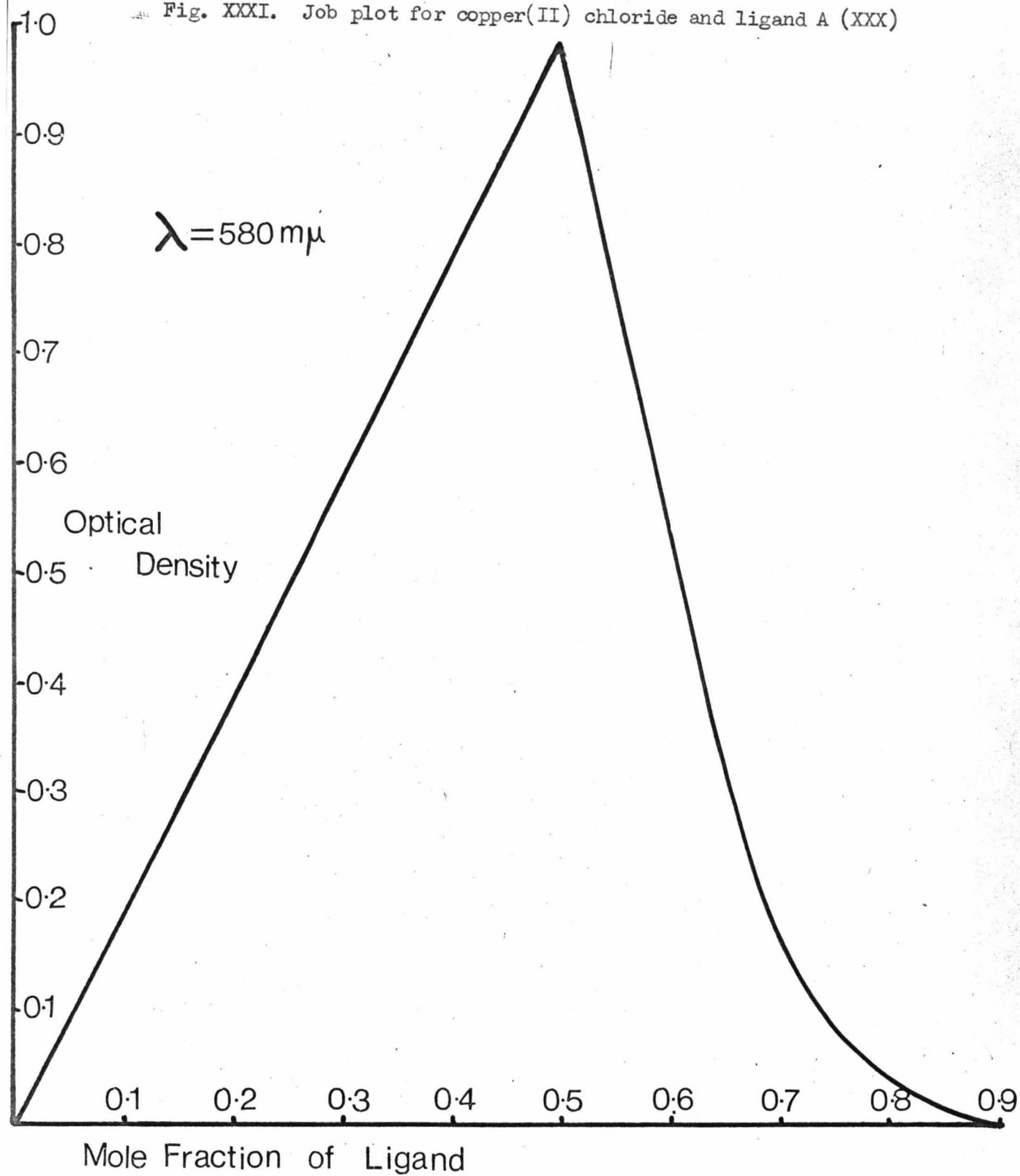
and it was found that the peak at 600 mμ quickly faded as the ligand concentration increased and did not reappear at any other wavelength. If one drop of pure ligand was added to the intense blue coloured solution, obtained by mixing equimolar amounts of copper(II) chloride and A (methanolic solution, 0.0066 molar), the colour immediately disappeared.

The solubility (with slow decomposition) of $CuACl_2$ allowed the solution spectra to be obtained:

water λ_{max} 17600 cm^{-1} ε = 186

aq-methanol

λ_{max} 16600 cm^{-1} ε = 186

aq-methanol (0.0066 molar) + 1 drop diethylamine

λ_{max} 16000 cm^{-1} ε = 186

These results show that the axial positions in the complex are very sensitive to solvent effects.

3.1(c) (iii) Magnetic data

TABLE 18

Magnetic susceptibilities of some nickel(II) and a copper(II) complex of A (XXX)

	$\chi_m \cdot 10^3$	$-\chi_D \cdot 10^3$	$\chi_{TIP} \cdot 10^3$	$\chi_m^{corr} \cdot 10^3$	μ_{eff}
NiA(SCN)$_2\frac{1}{3}$DMF	4.31	0.26	0.25	4.32	3.21$\pm$0.10
NiACl$_2$	3.78	0.20	0.24	3.74	2.99$\pm$0.10
CuACl$_2$	1.10	0.20	-	1.30	1.76$\pm$0.10

$(T = 298.2°K)$

These are in the range expected for paramagnetic octahedral
nickel(II) complexes and pseudo octahedral copper(II).

3.1(d) Comparison of "A" and 1,9-diamino 3,7-diazanonane (2,3,2 tet)

$$H_2NCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$$
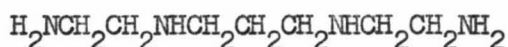
The chemistry of 2,3,2 tet has been investigated by Bosnich et al[68]
and by Milestone.[69] This ligand, unlike triethylenetetramine, can adopt
a _trans_ configuration with apparently no strain. Ligand "A" appears to be
able to do this also although the angle about the secondary amine groups
and the thioether groups will be different. The trimethylene bridge is
probably flexible enough to enable strain-free forms to exist. The
copper(II) 2,3,2 tet complexes absorb at higher wave number (~ 19000 cm^{-1})[68]
than does the complex Cu(A)Cl$_2$ (~ 14000 cm^{-1}) so the tetramine appears to
exert a stronger ligand field than does "A". As very little is known about
comparable thioether-secondary amine ligands it is not possible to say
whether this is typical or not. The solid nickel(II) complexes of 2,3,2 tet
are either paramagnetic (chloride, bromide and thiocyanate) or diamagnetic
(iodide and perchlorate).[68,69] All these complexes are expected to have
the organic residue in a plane. The two nickel(II) complexes of "A"
examined are paramagnetic.

Comparing the diffuse reflectance spectra:

Ni(2,3,2 tet)Cl$_2$ [69]	8200	13900	18100	27800
Ni(A)Cl$_2$		9800	16200	26000
Ni(2,3,2 tet)(SCN)$_2$ [69]		11000	18400	28600
Ni(A)(SCN)$_2\frac{1}{3}$DMF		11500	18700	29000

The ligand field strength in the (2,3,2 tet) chloride appears to be somewhat stronger than in $(A)Cl_2$; however, the thiocyanates appear to be about the same. Before any definite conclusions could be made many more complexes would need to be studied and also all the structures confirmed to be <u>trans</u>.

3.2 Complexes derived from 1,8-diamino 3,6-dithiaoctane "B" (XXXII)

$$H_2NCH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$$
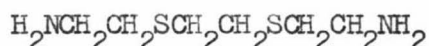
3.2(a) Preparation of the ligand "B"

The method used for ligand "A" (section 3.1(a)) was followed using 1,2-dibromoethane rather than 1,3-dibromopropane. The free base was obtained as a dark oil which did not solidify (Lit. M.P. 41-43°C[62]).

To 0.20 grams (0.00111 moles) of the amine "B" in hot ethanol was added 0.27 grams (0.00222 moles) of salicylaldehyde. The resulting yellow solution was heated briefly on a water bath and cooled. The bright yellow product (XXXIII x=y=2) was recrystallized from ethanol.

M.P. 104-105°C   (Lit. M.P. 107-108°C[62])

The salt B.2HCl was prepared by passing gaseous hydrogen chloride into a cooled ethanolic solution of the amine.

3.2(b) Complexes of "B" (XXXII)

3.2(b)(i) Attempted preparation of a nickel(II) complex

All attempts to prepare a complex failed, e.g.

Addition of a few drops of 0.880 ammonia to equimolar amounts of nickel(II) chloride hexahydrate and B.2HCl, in ethanol, produced an immediate mauve precipitate. The product was washed with ethanol and dried. The infrared spectrum was characteristic of a nickel(II) ammine and the product turned yellow-green on heating (loss of ammonia to give nickel(II) chloride). A similar attempt using diethylamine to liberate the free amine was also unsuccessful.

3.2(b)(ii) A copper(II) complex

To a solution of B.2HCl (3.0 grams, 0.0185 moles) in ethanol (150 mls) was added ca. 2-3 mls of 0.880 ammonia and then copper(II) acetate hydrate (2.365 grams, 0.0185 moles) dissolved in a little warm methanol. A solution of sodium perchlorate (10 grams), in ethanol, was then added to the deep royal blue solution and the mixture allowed to stand overnight. The solid material was removed by filtration and washed with methanol to remove the inorganic salts. The light blue product was washed with hot 2-propanol and dried in vacuo. The material was insoluble in all solvents tested (cold) and decomposed or remained insoluble when heated in those tried.

The analytical data for this complex was unsatisfactory, in that it could not be fitted to any simple structure (the insolubility suggests a

polymer). As the sample was impure and could not be recrystallized the infrared spectra was of little assistance in elucidating the possible structure.

3.3 Complexes derived from 1,5-bis(2-aminophenyl)-1,5-dithiapentane "C" (XXXIV)

3.3(a) Preparation of "C"

A solution of sodium (5.4 g, 0.23 gram-atoms) and 2-aminothiophenol (29 g, 0.23 moles) in 200 mls of absolute methanol was stirred and refluxed under nitrogen as 1,3-dibromopropane (22.9 g, 0.11 moles) in 10 mls of methanol was added dropwise. After the addition was complete (ca. 1 hour) the mixture was stirred and refluxed overnight and then allowed to cool. The precipitate of sodium bromide was removed by filtration and washed with methanol. To the filtrate was added the washings and then 30 mls (0.256 moles) of 48% hydrobromic acid. A precipitate formed rapidly. Yield = 23.0 grams.

On concentrating the filtrate a further 21 grams was obtained. Total yield = 44 grams (88%).

M.P. 189-191°C after recrystallization from methanol.

Analysis

Found   C 39.86%;   H 4.50%

$C_{15}H_{20}Br_2N_2S_2$ requires C 39.83%;   H 4.46%.

3.3(b) Metal complexes of "C" (XXXIV)

A sample of the free base did not react with aqueous nickel(II) acetate when the two were heated on a water bath. To prepare a nickel(II) complex the following procedure was used:

To 1.5 grams (0.0033 moles) of C.2HBr in anhydrous ethanol was added 0.68 grams (0.0066 moles) of triethylamine. To this solution was added anhydrous nickel(II) chloride (0.50 grams, 0.0033 moles) in anhydrous ethanol. The mixture was stirred for two days and the pale green product obtained, washed with dry ethanol and then with sodium dried ether.

Analysis

Found C 35.87%; H 3.99%; Ni 11.47%.

$NiC_{15}H_{18}Br_2N_2S_2$ requires C 35.40%; H 3.56%; Ni 11.53%

3.3(c) <u>Spectral data</u>

<u>TABLE 19</u>

$Ni(C)Br_2$

(i) Electronic (cm^{-1}) (solid state)

| 29000 | 154000 | 10000 |

(ii) Infrared

J_{NH_2} 3333 s,sp $J_{C\cdots C}$ 1595 s,sp
3265 s,sp   1587 sh
3172 s,sp

δ_{NH_2} 1556 s,sp

J_{CH} aromatic

δ_{CH_2} antisym.   1475 s,sp
3150 sh
3110 s,sp δ_{CH} orthodisubst.   765 s,sp
3080 s,sp   754 s,sp

J_{CH} aliphatic ρ_{CH_2} 711 m,sp
2930 w,sp
2915 w,sp
2911 w,sp

C. 2HBr

Large number of bands 2470 to 3150 cm^{-1} $J_{NH_3^+}$, J_{CH}

$J_{C\cdots C}$ 1604 w,sp
1580 m,sp

$\delta_{NH_3^+}$ 1548 s,sp

δ_{CH} 779 s,sp
759 s,sp

3.3(d) <u>Magnetic Susceptibility</u>

$$\chi_m^{corr} = 4.32 \times 10^{-3} \text{ c.g.s.}$$

$$\mu_{eff} = 3.20 \pm 0.10 \text{ B.M.}$$

The magnetic and electronic spectral data are typical of a octahedral paramagnetic nickel(II) complex.

3.3(e) <u>Some comments regarding A, B, C and related systems</u>

It was found that B did not react with nickel(II) under all the conditions used and C did so only under rigorously anhydrous conditions. The reasons for this are not clear but it is probably a steric problem. However both these ligands formed complexes with copper(II) (unfortunately these were not obtained in a pure state), and this may be because of the greater affinity of copper(II) for sulphur.

Gonick et al[70] reported the formation constants of Ni(II) with B ($-\Delta G = 10.9$ Kcal.mole^{-1} at $30^\circ C$), however in a later paper, from the same Chemistry Department, this ligand was reinvestigated and no mention was made of a nickel(II) complex.[71]

It is helpful to consider some comments regarding similar sulphur-nitrogen systems.[72] With regard to the metal complexes of 1,8 bis($\propto$-pyridyl) 3,6-dithiaoctane (XXXVa) and 1,6 bis($\propto$-pyridyl) 2,4-diazahexane (XXXVb) it has been suggested that it is possible that the former does not form strain-free planar complexes owing to the larger size of sulphur compared to nitrogen. The ligands of structure (XXXIII) x = 2 or 3, y = 2 or 3 can form practically strainless sexadentate complexes.

However when x=2=y the N-S-S-N system cannot lie in one plane as the bonds from the sulphur atoms must be pyramidally orientated. Only when y=3 is it possible to have a N-S-S-N coplanar arrangement as then the trimethylene bridge is flexible enough to allow this situation.

With ligand C the aromatic ring holds the N-S system to a single plane and because there is strain induced when the sulphurs coordinate the result is a weakly coordinated complex. It must be because of the coordinating angles of the sulphurs that does not allow ligand B to coordinate (cf. triethylene tetramine which prefers a non-planar arrangement with nickel(II)).

A search through the literature has revealed some examples of ligands that do and do not chelate with nickel(II):

$$HSCH_2CH_2SCH_2CH_2SCH_2CH_2SH$$
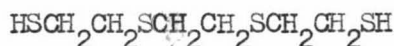
(cf. ligand B) does not[10], however

$$HOOCCH_2SCH_2CH_2SCH_2COOH$$
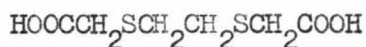
forms chelate complexes with nickel(II) readily.[73]

The ligand:
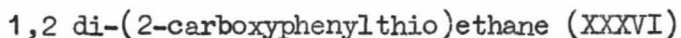
1,2 di-(2-carboxyphenylthio)ethane (XXXVI) coordinates readily in aqueous solution to nickel(II).[74] This is probably so (in relation to C), because the carboxyl group introduces another atom in the chelate ring and allows departure from coplanarity of the O-S system. In the class of tridentate ligands it is found that:

$$H_2NCH_2CH_2NHCH_2CH_2NH_2 \quad [75]$$
$$H_2NCH_2CH_2SCH_2CH_2NH_2 \quad [5]$$

$$HSCH_2CH_2SCH_2CH_2SH_2 \quad [10]$$
$$HSCH_2CH_2N(CH_3)CH_2CH_2NH_2 \quad [10]$$
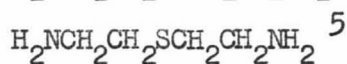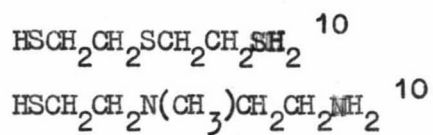
all form chelate complexes with nickel(II) but

$$HSCH_2CH_2NHCH_2CH_2SH \quad [10]$$

does not.

There has been little work done specifically intended to investigate the steric requirements of the thioether donor group and so it is difficult to offer explanations for unusual behaviour.

PART 4   SOME REACTIONS OF COORDINATED LIGANDS

4.1 Introduction

In this section two types of reaction were used to modify coordinated amino and thiol groups.

(a) The acetone condensation reaction, extensively investigated by Curtis[21]:
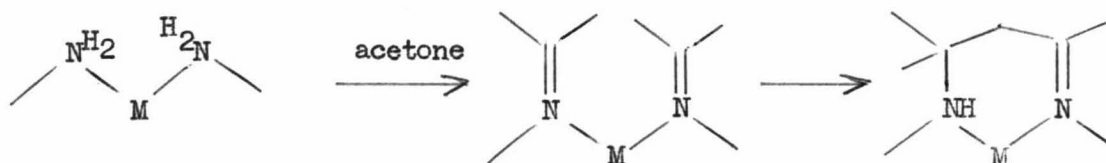
(b) The reaction of coordinated thiols with alkylhalides, extensively investigated by Busch[19]:
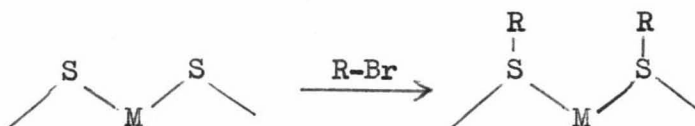
These two reactions were used in attempts to prepare bridged complexes and macrocycles.

4.2 The reaction of a nickel(II) complex of 2-(benzylthio)ethylamine with acetone

To a solution of nickel(II) acetate tetrahedrate (0.25 grams, 0.001 moles), ammonium thiocyanate (0.15 grams, 0.002 moles) and 2-(benzylthio)ethylamine (0.33 grams, 0.002 moles) in a little warm methanol was added 50 mls of acetone. After refluxing the mixture for 3 hours and cooling overnight the solution was evaporated to a small volume and 2-propanol added. A pale blue solid (0.33 grams) was obtained and recrystallized from 2-propanol.

Analysis:

Found Ni 9.97%;　C 53.10%;　H 6.02%

$NiC_{26}H_{34}N_4S_4$ requires Ni 9.95%;　C 52.97%;　H 5.81%.

TABLE 20

Infrared data for the product $NiC_{26}H_{34}N_4S_4$ obtained in the

above reaction

(all values cm^{-1})

ν_{NH}	3250 w,sp	δ_{CH_2} antisym.	1453 s,sp
	3190 m,sp	δ_{CH_3} gem	1365 m,sp
ν_{CH} aromatic	3075 w,sp		1378 m,sp
	3060 w,sp	ν_{C-S}	795 w,sp
	3025 w,sp	δ_{CH} aromatic	775 s,sp
ν_{CH} aliphatic	2970 m,sp		705 s,sp
	2935 sh		
	2920 m,sp		
	2875 w,sp		
$\nu_{C\equiv N}$	2065 s,sp		
$\nu_{C=N}$	1667 s,sp		
	1646 s,sp		
$\nu_{C=C}$ aromatic	1602 m,sp		
	1583 w,sp		
	1495 s,sp		

Complexes containing the 2-iminopropane and 2-amino 2-methyl 4-iminopentane residues are hydrolysed by aqueous potassium cyanide. The products of this reaction are the ketones acetone and mesityloxide

respectively together with the metal complex of the amine. The
reaction is illustrated in Fig. (XXXVII). The usual procedure is to
steam distil a mixture of the complex and aqueous KCN, the vapours being
passed into a solution of 2,4 dinitrophenylhydrazine. With the complex
$NiC_{26}H_{34}N_4S_4$ neither the pure mesityloxide nor the pure acetone
2,4 dinitrophenylhydrazone was obtained. It appears probable that the
complex was a mixture of the bridged and unbridged species as the infrared
showed $\int_{NH}$ and two $\int_{C=N}$ bands.

4.3 Attempted cyclisations of complexes of A (XXX) and B (XXXII)

The nickel(II) chloro complex of A was quite insoluble in acetone
even in a sealed tube at $160^{o}C$. No reaction was observed apart from some
tarry decomposition products. The nickel(II) thiocyanato complex was
insoluble in cold acetone and decomposed when heated in this reagent. The
copper(II) chloro complex of A also decomposed rapidly when heated in
acetone.

The uncharacterized copper(II) complex of B (Sect. 3.2) reacted
readily when boiled in acetone containing a few drops of pyridine. The
pale-green solid (λ_{max} 14,200 cm^{-1}, cf. $Cu(B)^{2+}\lambda_{max}$ 15,800 cm^{-1}, (solid
state reflectance)) was washed with acetone before analysis. The infrared
spectrum did not indicate $\int_{NH}$ and had broad absorption at 1625 cm^{-1}
which may be attributable to $\int_{C=N}$. The I.R. indicated that the sample
was pure but as with the case with CuB^{2+} no structure could be assigned
in accordance with the analytical data. The complex on standing in
acidic 2,4 dinitrophenylhydrazine gave the pale yellow acetone

2,4 dinitrophenylhydrazone. It is possible then that the primary amino groups reacted to give N-isopropylidene groups.

4.4 A reaction of coordinated thiol

Busch et al[16,17] have studied the reaction of (VII) Z = N-CH$_3$ with benzylbromide and methyl iodide. The compound (VII) Z = S was prepared and reacted with benzylbromide to see if Busch's conclusions are in accord with the behaviour of this complex.

Preparation of 2,2' dithiodiethylsulphide   HSCH$_2$CH$_2$SCH$_2$CH$_2$SH

2,2' dihydroxydiethylsulphide, HOCH$_2$CH$_2$SCH$_2$CH$_2$OH, was prepared from 2-chloroethanol and sodium sulphide nonahydrate[76]

Yield: 42g of a yellow syrup

B.P. 160-170°C (10 mm)

Lit. B.P. 164-166°C (20 mm),

and 40 g of undistillable black oil. To this oil was added 61 grams of thiourea and 100 mls of concentrated hydrochloric acid. The mixture was refluxed for 30 mins.[77] A solution of sodium hydroxide (60 grams, 1.5 moles) in 350 mls of water was added and the mixture refluxed, under nitrogen, for one hour. After cooling 100 mls of concentrated hydrochloric acid was added to liberate the free thiol. The sulphide was extracted into ether and after drying, distilled.

Yield: 29.8 g.

B.P. 144-148°C (16-20 mm)

Lit. B.P. 135-137°C (18 mm)[10].

Infrared:

J_{CH} 2935 s,sp

           2915 s,sp

           2825 m,sp

J_{SH} 2540 s,sp

δ_{CH} 1435 s,sp

           1418 s,sp

The nickel(II) complex was prepared[10] in 65% yield. The crystals which were obtained after recrystallization from chloroform were diamagnetic and pitch black.

Analysis:

Found C 22.77%; H 3.68%

$Ni_2C_8H_{16}S_6$ requires C 22.76%; H 3.82%.

The zeromagnetic moment and analysis are in accord with the proposed structure ((VII) X = S).

Reaction with Benzylbromide

To 1.30 grams (0.00294 moles) of the nickel complex in 200 mls of chloroform was added 2 mls (0.0081 moles) of benzylbromide. The solution was stirred overnight during which time it changed in colour from deep red to dark brown. The solution was concentrated to a small volume and the solid precipitated by the addition of sodium dried ether. The complex was recrystallized by dissolving it in   dichloromethane and adding diethylether.

Analysis:

Found C 35.36%; H 4.05%; Ni 15.52%

$Ni_2C_{22}H_{30}S_6Br_2$ requires C 34.58%; H 3.96%; Ni 15.36%.

Infrared:

$\displaystyle\smallint_{CH}$ aromatic   3075 vw,sp

                            3055 w,sp

                            3020 w,sp

$\displaystyle\smallint_{CH}$ aliphatic   2950 vw,sp

                            2910 m,sp

$\displaystyle\smallint_{C=C}$ aromatic   1602 w,sp

                            1583 vw,sp

                            1496 s,sp

δ_{CH_2} antisym.   1452 s,sp

δ_{CH} aromatic   768 m,sp

                            698 s,sp

Magnetic Susceptibility:

$$\chi_m^{corr.} = 0.922 \times 10^{-3} \text{ c.g.s.}$$

$$\mu_{eff} = 1.48 \pm 0.10 \text{ B.M.}$$

The value of μ is in accord with the proposed structure in which there are two bromides for two nickels, the exact location of the halogens is not known. Busch also found magnetic moments of about this magnitude for complexes (VIII) X = $N-CH_3$.

The fact that only two benzyl molecules are attached indicates that only two of the six sulphurs in the molecule are alkylated. Rate

studies[19] indicate that the non-bridging thiols are reactive and in this case neither the bridging thiols nor the thioether groups have reacted.

The mechanisms of this type of reaction have been studied.[17,78] The low activation energies (7-12 Kcal.mole^{-1}) indicate that the metal-sulphur bond is not broken in the rate determining step. The most favoured mechanism is that in which the benzyl bromide is coordinated to the nickel in a pre-equilibrium step and then in the rate determining step there is a nucleophilic attack by the sulphur on the benzyl group. The reactions are first order in both metal complex and benzyl bromide over limited concentration ranges.

4-5 An unsuccessful attempt to prepare a macrocycle

Busch and Thompson[18] prepared complexes (IX) and attempted to ring close them by reaction with dihalides. To determine if reduction of the unsaturated five membered ring would enable the closure reaction to proceed with 1,3 dibromopropane the complex (IX) R' = CH$_3$ was prepared.[24] Attempted reduction with sodium borohydride was not successful. No other reduction methods were tried.

PART 5   AN S-DETRITYLATION REACTION

5.1   2-(triphenylmethylthio)ethylamine

During the course of this work an S-trityl derivative of 2-amino
ethane thiol was prepared (it was intended to use the trityl group as an
S-protecting agent),

5.1(a)   Preparation of 2-(triphenylmethylthio)ethylamine $Ph_3CSCH_2CH_2NH_2$

Triphenylmethanethiol was prepared in almost quantitative yield by
the reaction of H_2S with triphenylmethanol in glacial acetic acid.[79] The
thiol was recrystallized from methanol.   2-(triphenylmethylthio)ethylamine
was prepared[80] from the sodium salt of triphenylmethane thiol and 2-bromo-
ethylamine in 72.5% yield.

M.P. 88-89°C (Lit. M.P. 90°)[80]

5.1(b)   Reaction with nickel(II)

To a solution of nickel(II) chloride hexahydrate (2 grams) in
100 mls of methanol added 4 grams of $Ph_3CSCH_2CH_2NH_2$. The solution was
warmed on a water bath. After two mins. the solution had turned brown but
the heating was continued for one hour. The mixture was cooled and the
brown insoluble solids removed by filtration and the filtrate evaporated
to a small volume. Water was added and the mixture warmed for a short period
and then allowed to cool. The white solid obtained was removed and dried.

The infrared spectrum had bands characteristic of both
triphenylmethanol and 2-(triphenylmethylthio)ethylamine. It appears that a
very long time may be necessary for the reaction to go to completion and the

rapid development of the brown colour is deceiving because the complex formed has a very intense colour detectable at low concentrations.

5.2 NN'-bis[2-(triphenylmethylthio)ethyl]1,3 diaminopropane

$$Ph_3CSCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2SCPh_3$$
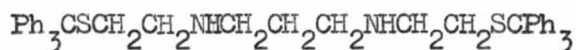
5.2(a) Preparation

The ligand, as the di-hydrobromide, was prepared from 2-(triphenylmethylthio)ethylamine and 1,3 dibromopropane, in toluene, in 76% yield.

M.P. 193-195°C decomp.

Analysis:

Found: C 65.17%; H 5.99%; Br 18.43%.

$C_{45}H_{48}Br_2N_2S_2$ requires C 64.28%; H 5.75%; Br 19.18%.

This ligand reacted with nickel(II) with loss of the trityl groups to form a complex of:

$HSCH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2SH$ (NN'-bis(2-thioethyl)1,3 diaminopropane)
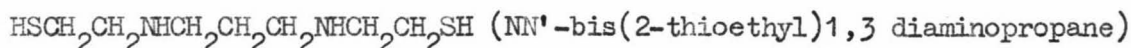
which is an isomer of ligand "A" (XXX). A nickel(II) complex of this ligand is interesting in that it may be possible to ring close it using the coordinated thiol-alkyl halide reactions discussed in section 4.

5.2(b) Reaction of the S-trityl derivative with nickel(II) acetate

A solution of the dihydrobromide of the ligand NN'-bis[2-(triphenylmethylthio)ethyl]1,3 diaminopropane (5.00 grams, 0.006 moles) and nickel(II) acetate tetrahydrate (1.48 grams,

0.006 moles) in methanol (100 mls) was refluxed for two hours. The green solution rapidly darkened and after two hours was quite black. On standing at room temperature for three days, in a stoppered flask, the reaction mixture had deposited a mass of small black crystals on the walls of the vessel. This product was removed, washed with methanol and dried in vacuo.

Analysis:

Found C 23.55%; H 4.74%; Ni 24.62%

$Ni_3C_{14}H_{32}N_4S_4Br_2$ requires C 23.33%; H 4.48%; Ni 24.43%.

A probable structure is (XXXVIII). The complex is diamagnetic indicating that, as in the case of complexes of type (IV) the thiol sulphurs stabilize the spin paired state of all three nickel atoms.

Unfortunately the complex refused to dissolve in all the solvents tried (it could be boiled in dimethylformamide with no effect) and the attempted reactions with dihalides were not possible.

PART 6   APPENDICES

APPENDIX 1

As an estimate of the degree of tetragonal distortion the visible spectra of the complexes of 2-(benzylthio)ethylamine may be compared with the values predicted by the Liehr-Ballhausen energy level diagram,[7] Fig. XXXIX, which assumes purely octahedral symmetry and includes a consideration of spin-orbit coupling, a spin-orbit coupling constant of 275 cm^{-1} (free ion value 315 cm^{-1}) being used.

In Table 21 the calculated and observed values are indicated. The 10Dq parameter was obtained from the complexes themselves.

TABLE 21

Comparison of observed energies of absorption bands of the nickel(II) complexes (XXV) with theoretical values for octahedral symmetry obtained from Fig. XXXIX. (Energies in cm^{-1}).

		J_1	J_2	J_3
Ni(amine)$_2$Cl$_2$	calc.	10,000-10,500	16,000-17,000	26,000-26,500
	obs.	10,300	16,500	25,700
(NO$_3$)$_2$	calc.	9,000-9,500	14,500-15,500	25,000-25,500
	obs.	10,900;7,900	16,700	26,900
(SCN)$_2$	calc.	8,500-9,000	13,500-15,000	24,000
	obs.	8,900	18,000	28,300
I$_2$	calc.	8,000-9,000	13,000-14,000	23,500
	obs.	9,800;7,400	15,900	24,500
*(NO$_2$)$_2$	calc.	11,500-12,000	18,000-19,000	29,000
	obs.	11,600	20,400	26,700

* On this diagram no assignment could be made of the peak at 15,700 cm^{-1}.

FIG. 10-17. Energy-level diagram for $(3d)^8$ with spin-orbit coupling included. The labeling is that of the double group. The hole formalism has been used.
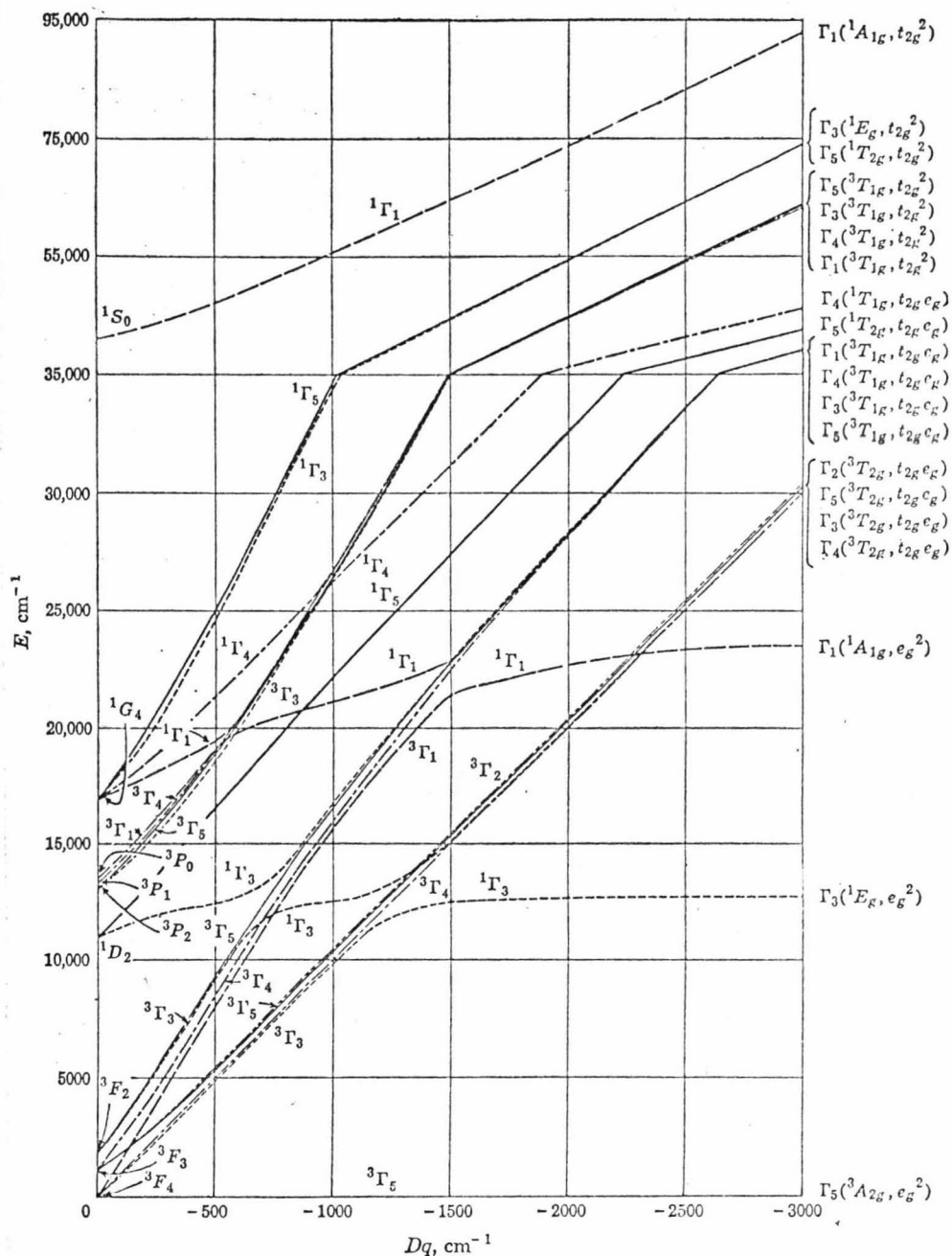
Fig. XXXIX

The splitting of $\sqrt{}_1$ in the nitro and iodo complexes is too large to be due to spin-orbit coupling and the peaks are also too far apart for one to be assigned a ${}^3A_{2g}(F)$ —— ${}^1E_g(F)$ transition.

The deviation of the complexes from purely cubic to tetragonally distorted symmetry can further be estimated by a method due to Bostrup and Jorgensen,[81] in which the differences between the ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ levels in the complexes, (X_{obs}), is compared with the value, (X_{calc}), calculated via the interelectronic repulsion parameter B and the ligand field strength 10Dq.

$$15B = (\sqrt{}_2 + \sqrt{}_3)_{obs} - 30Dq \qquad \text{eqn. 1}$$

$$(\sqrt{}_3 - \sqrt{}_2)_{calc} = X_{calc} = (225B^2 - 180BDq + 100Dq^2)^{\frac{1}{2}} \qquad \text{eqn. 2}$$

(Both these equations are obtained from the secular determinants of the $3d^8$ system, equation 2 is the difference between the two roots of

$$\begin{vmatrix} 3B + 8Dq - E & 6B \\ 6B & 12B-2Dq-E \end{vmatrix} = 0)$$

TABLE 22

Calculated and observed energy differences between the $^3T_{1g}(F)$ and $^3T_{1g}(P)$ levels in some nickel(II) complexes of 2-(benzylthio) ethylamine (XXV). (Energies in cm^{-1}).

	$10Dq^a$	$15B^b$	X_{calc}^c	X_{obs}^a	$X_{calc} - X_{obs}$
Ni(amine)$_2$Cl$_2$	10,300	12,400	10,300	10,300	0
(NO$_3$)$_2$	9,400	15,400	12,300	10,200	2,100
(SCN)$_2$	8,900	19,600	15,900	10,300	5,600
I$_2$	8,600	14,600	11,700	8,600	3,100
(NO$_2$)$_2$	11,600	12,300	10,700	6,300	4,400

(a) Table 8; (b) eqn. 1; (c) eqn. 2

Apart from the chloro complex the distortion deduced by this method appears to be considerable. This method does not consider the effect of spin-orbit coupling but this is such that the band multiplets cover a range of no more than 1,000 cm^{-1} and this spread would not be large enough to reduce $(X_{calc} - X_{obs})$ down to two or three hundred wave numbers which is expected from complexes of nearly perfect cubic symmetry. The thiocyanato complex is very distorted on this model and this distortion supports the previously proposed cis (anion) configuration for this complex.

APPENDIX 2

Data for Job plot (Fig. XXXI)

λ = 580 mμ (17,250 cm^{-1})

x	1-x	$D_{meas.}$	D_M	Y
0.0	1.0	0.003	0.003	0
0.1	0.9	0.174	0.003	0.1737
0.2	0.8	0.362	0.003	0.3618
0.3	0.7	0.569	0.003	0.5688
0.4	0.6	0.774	0.003	0.7738
0.5	0.5	0.983	0.003	0.9828
0.6	0.4	0.540	0.003	0.5399
0.7	0.3	0.169	0.003	0.1689
0.8	0.2	0.040	0.003	0.0399
0.9	0.1	0.009	0.003	0.0089
1.0	0.0	0.000	0.003	0

λ = 600 mμ (16,650 cm^{-1})

x	1-x	$D_{meas.}$	D_M	Y
0.0	1.0	0.0055	0.0055	0.0
0.1	0.9	0.185	0.0055	0.1845
0.2	0.8	0.382	0.0055	0.3816
0.3	0.7	0.591	0.0055	0.5906
0.4	0.6	0.804	0.0055	0.8037
0.5	0.5	1.230	0.0055	1.2297
0.6	0.4	0.560	0.0055	0.5598
0.7	0.3	0.175	0.0055	0.1748
0.8	0.2	0.040	0.0055	0.0399
0.9	0.1	0.009	0.0055	0.0089
1.0	0.0	0.00	0.0055	0.0

λ = 625 mμ (16,000 cm^{-1})

x	1-x	$D_{meas.}$	D_M	Y
0.0	1.0	0.013	0.013	0
0.1	0.9	0.189	0.013	0.1773
0.2	0.8	0.376	0.013	0.3656
0.3	0.7	0.582	0.013	0.5734
0.4	0.6	0.850	0.013	0.8422
0.5	0.5	1.240	0.013	1.2335
0.6	0.4	0.545	0.013	0.5398
0.7	0.3	0.169	0.013	0.1651
0.8	0.2	0.033	0.013	0.0304
0.9	0.1	0.008	0.013	0.0067
1.0	0.0	0.00	0.013	0.00

REFERENCES

1. R. G. Pearson, J. Amer. Chem. Soc., 85, 3533 (1963).

2. S. Ahrland, J. Chatt and N. R. Davies, Quart. Rev., 12, 265 (1958).

3. American Cyanamid European Research Institute: Symposium.
   Chem. & Eng. News, May 31 (1965), p.90.

4. S. E. Livingstone, Quart. Rev., 19, 386 (1965).

5. C. K. Jorgensen, J. Inorg. Nucl. Chem. 24, 1571 (1962).

6. R. L. Carlin and E. Weissberger, Inorg. Chem., 3, 611 (1964).

7. A. D. Liehr and C. J. Ballhausen, Ann. Phys. (N.Y.), 6, 134 (1959).

8. D. C. Jicha and D. H. Busch, Inorg. Chem., 1, 872 (1962).

9. R. L. Girling and E. L. Amma, Inorg. Chem., 6, 2009 (1967).

10. J. Harley-Mason, J. Chem. Soc., 146 (1952).

11. D. L. Leussing, J. Amer. Chem. Soc., 82, 4458 (1960).

12. D. C. Jicha and D. H. Busch, Inorg. Chem., 1, 878 (1962).

13. C. A. Root and D. H. Busch, Inorg. Chem., 7, 789 (1968).

14. C. W. Blomstrand, Z. prakt. chem., 38, 529 (1888); Brit. Chem. Abs.
    56, 230 (1889).

15. P. C. Ray and P. C. Guha, J. Chem. Soc., 115, 1148 (1919).

16. D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathal and E. Blin,
    J. Amer. Chem. Soc., 86, 3642 (1964).

17. D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson and M. L. Morris,
    Advances in Chemistry, Series No.37, American Chemical Society,
    Washington D.C. (1963), p.125.

18. M. C. Thompson and D. H. Busch, J. Amer. Chem. Soc., 86, 3651 (1964).

19. D. H. Busch, Record Chem. Progr. 25, 107 (1964).

20. G. R. Brubaker and D. H. Busch, Inorg. Chem., 5, 2114 (1966).

21. N. F. Curtis, Coord. Chem. Rev., 3, 3 (1968).

22. G. A. Melson and D. H. Busch, J. Amer. Chem. Soc., 86, 4834 (1964).

23. M. Green and P. A. Tasker, Chem. Comm., 518 (1968).

24. M. C. Thompson and D. H. Busch, J. Amer. Chem. Soc., 86, 213 (1964).

25. H. Jadamus, Q. Fernando and H. Freiser, Inorg. Chem., 3, 928 (1964).

26. Ibid., J. Amer. Chem. Soc., 86, 3056 (1964).

27. L. F. Lindoy and S. E. Livingstone, Inorg. Chem. Acta 1, 365 (1967).

28. Q. Fernando and P. J. Wheatley, Inorg. Chem. 4, 1726 (1965).

29. L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, Inorg. Chem.,
    6, 652 (1967).

30. Ibid., Australian J. Chem., 19, 1391 (1966).

31. L. Sacconi and G. P. Seroni, Inorg. Chem., 7, 295 (1968).

32. R. J. Gaul and W. J. Fremuth, J. Org. Chem., 25, 869 (1960).

33. E. Walton, A. N. Wilson, F. W. Holly and K. Folkers, J. Amer. Chem. Soc.,
    76, 1146 (1954).

34. F. Cortese, Organic Synthesis, Coll. Vol. II p.91
    J. Amer. Chem. Soc., 58, 191 (1936).

35. J. Baddiley and E. M. Thain, J. Chem. Soc., 800 (1952).

36. J.C.D. Brand and G. Eglinton, "Applications of Spectroscopy to Organic
    Chemistry", Oldbourne Press (London) (1965), Cpt. IV.

37. K. Nakamoto, "Infrared Spectra of Coordination Compounds", Wiley
    (New York) (1963) pt. III.

38. J. Lewis, R. S. Nyholm and P. W. Smith, J. Chem. Soc., 4590 (1961).

39. N. F. Curtis and Y. M. Curtis, Inorg. Chem., 4, 804 (1965).

40. D. F. Cook, Thesis, Victoria University of Wellington (1967).

41. L. EI-Sayed and R. O. Ragsdale, *Inorg. Chem.*, 6, 1640 (1967).

42. R. B. Penland, T. J. Lane, J. V. Quagliano, *J. Amer. Chem. Soc.*, 78, 887 (1956).

43. D.M.L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

44. A. Sabatini and I. Bertini, *Inorg. Chem.* 4, 959 (1965).

45. D. M. Adams, "Metal-Ligand and Related Vibrations", Arnold (1967).

46. G. E. Coates and C. Parkin, *J. Chem. Soc.* 421 (1963).

47. J. Pluscec and A. D. Westland, *J. Chem. Soc.*, 5371 (1965).

48. K. Nakamoto, "Advances in the Chemistry of Coordination Compounds", ed. S. Kirschner, MacMillan, New York (1961), p.437.

49. C. C. Addison and M. Kilner, *J. Chem. Soc.* (A) 1249 (1966).

50. C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes" Pergamon (1964), Cpt. 7.

51. T. M. Dunn, "Modern Coordination Chemistry", ed. Lewis and Wilkins, Interscience (1960).

52. L. E. Orgel, "An introduction to Transition Metal Chemistry" Methuen (1963), p.88.

53. D. S. McClure, *Solid State Physics*, 9, 399 (1959).

54. G. Maki, *J. Chem. Phys.* 28, 651 (1958); Ibid. 29, 162 (1958).

55. A.B.P. Lever, *Coord. Chem. Rev.*, 3, 119 (1968).

56. B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

57. N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

58. P. C. Selwood, "Magnetochemistry", Interscience (1956).

59. B. N. Figgis, "Introduction to Ligand Fields", Interscience (1966).

60. B. N. Figgis and J. Lewis, _Prog. Inorg. Chem._, 6, 37 (1964).

61. M. E. Elliot and B. J. Hathaway, _Inorg. Chem._, 5, 885 (1966).

62. F. P. Dwyer, F. Lions and D. P. Mellor, _J. Amer. Chem. Soc._, 72
    5037 (1950).

63. B. J. Brisdon, _Inorg. Chem._, 6, 1791 (1967).

64. M. L. Larson and F. W. Moore, _Ibid_, 5, 801 (1966).

65. F. A. Cotton and N. F. Curtis, _Ibid_, 4, 241 (1965).

66. R. S. Drago, D. W. Meek, M. D. Joesten and L. LaRoche, _Ibid_, 2, 124 (1963).

67. W. C. Vosburgh and G. R. Cooper, _J. Amer. Chem. Soc._, 63, 437 (1941).

68. B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb,
    J. Chem. Soc. (A), 1331 (1966).

69. N. B. Milestone, Thesis, Victoria University of Wellington, 1969.

70. E. Gonick, W. C. Fernelius and B. E. Douglas, _J. Amer. Chem. Soc._,
    76, 4671 (1954).

71. G. H. McIntyre, B. P. Block and W. C. Fernelius, _J. Amer. Chem. Soc._,
    81, 529 (1958).

72. H. A. Goodwin in "Chelating Agents and Metal Chelates", Cpt. 4.
    Ed. F. P. Dwyer and D. P. Mellor, Academic Press (1964).

73. K. Suzuki and K. Yamasaki, _J. Inorg. Nucl. Chem._, 24, 1093 (1962).

74. S. E. Livingstone, _J. Chem. Soc._, 1042 (1956).

75. N. F. Curtis and H.K.J. Powell, _J. Chem. Soc._ (A) 3069 (1968).

76. E. M. Faber and G. E. Miller, _Org. Syn._ Coll. Vol. II, p.576.

77. E. E. Reid, "Organic Chemistry of Bivalent Sulphur", Vol. I,
    Chemical Publishing Co. (1955).

78.   E. L. Blin and D. H. Busch, <u>J. Amer. Chem. Soc.</u>, <u>90</u>, 4280 (1968).

79.   M. P. Balfe, J. Kenyon and C. E. Searle, <u>J. Chem. Soc.</u> 3309 (1950).

80.   F. J. Carroll, H. M. Dickson and M. E. Wall, <u>J. Org. Chem.</u> <u>30</u>, 33 (1965).

81.   O. Bostrup and C. K. Jorgensen, <u>Acta Chem. Scand.</u>, <u>11</u>, 1223 (1957).

ACKNOWLEDGEMENTS
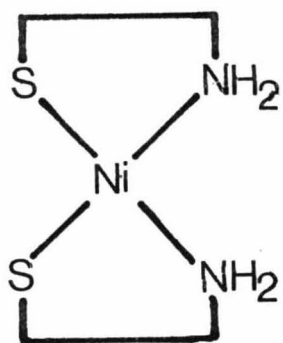
I
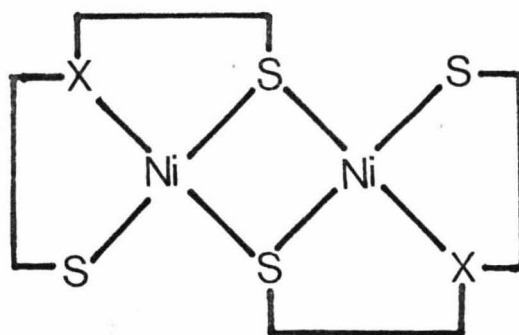
II

X = S, N—CH₃
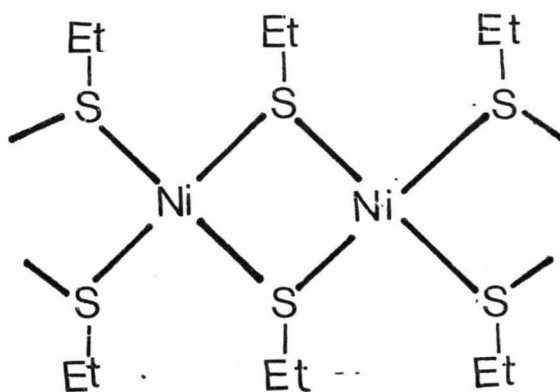
III
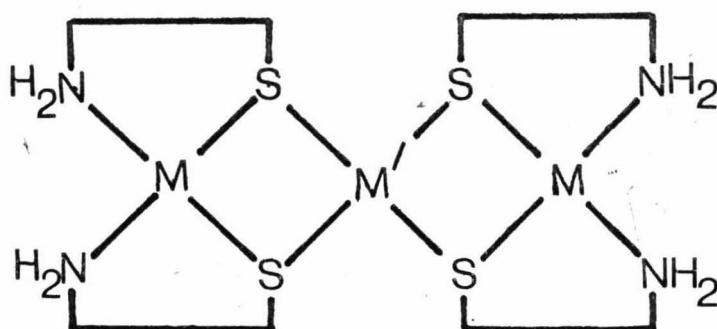
IV

M = Pd(II), Ni(II)

M′ = M, Cu(I), Cu(II), Cd(II), Pt(II)

$$Z = N - CH_3$$

$$R = CH_3 \ \& \ C_6H_5CH_2$$

I

XIII

$Ni(en)_3^{2+} + CH_3COCH_3 \longrightarrow$

XIV

XV

XVI
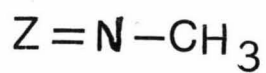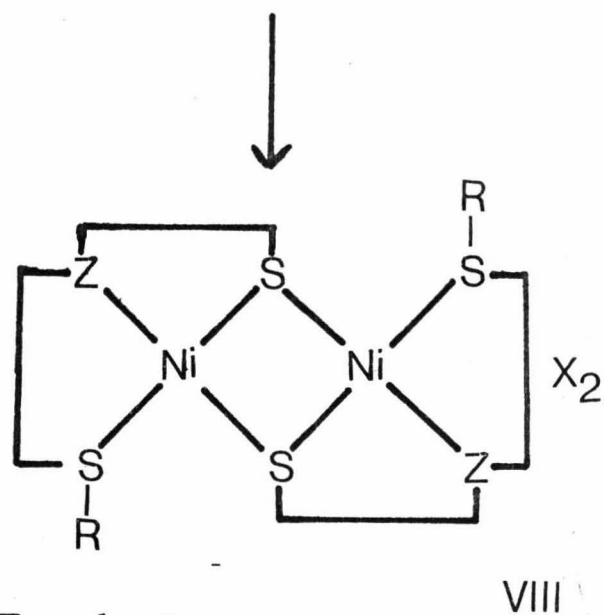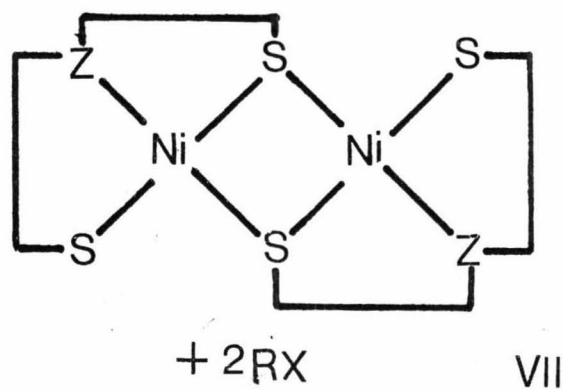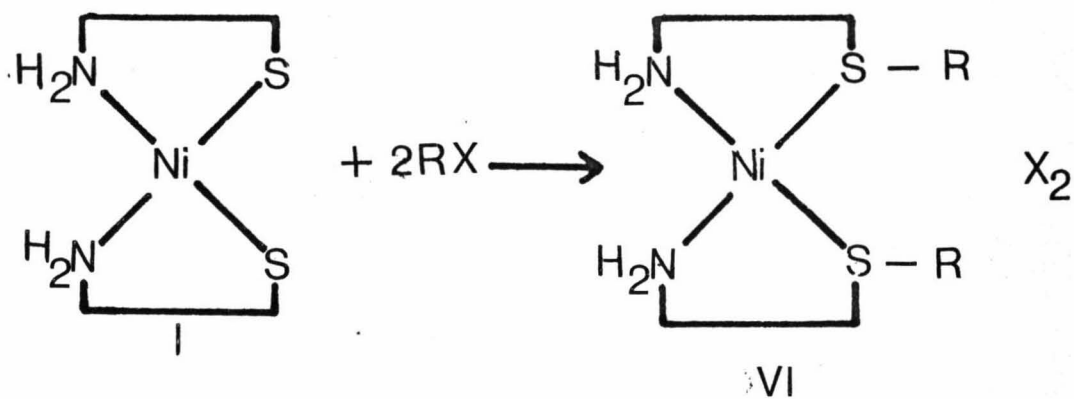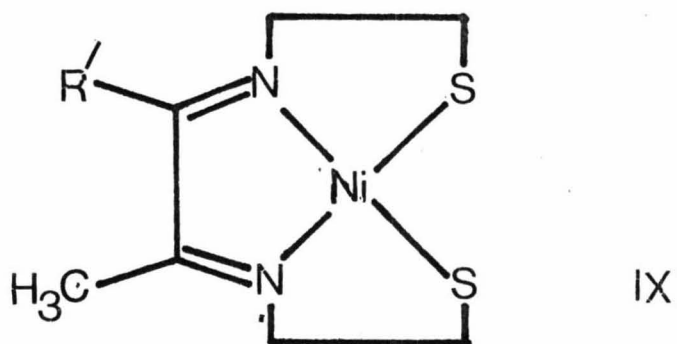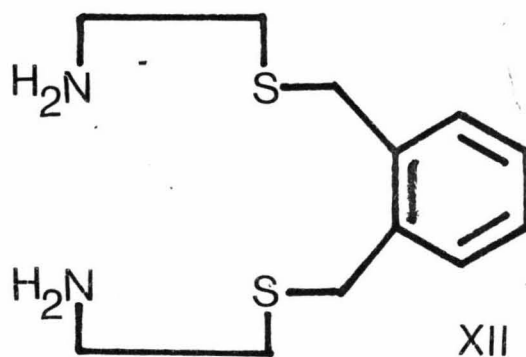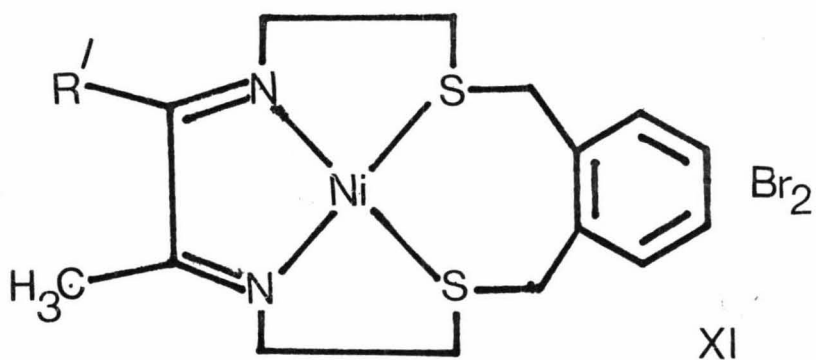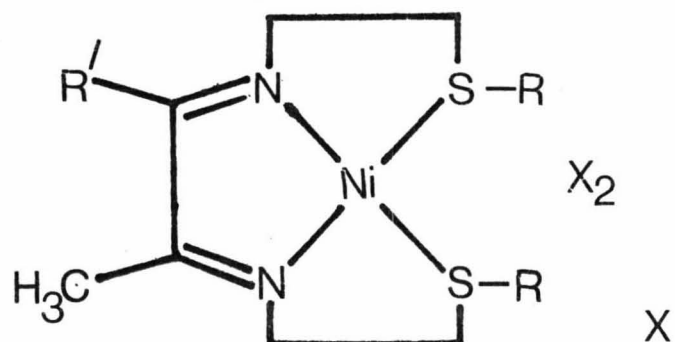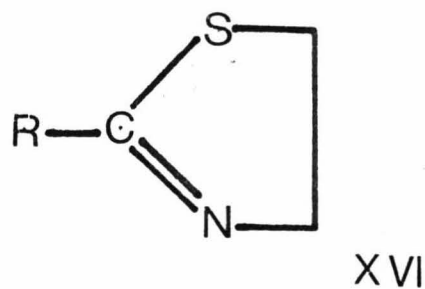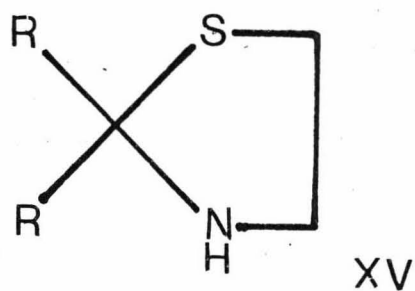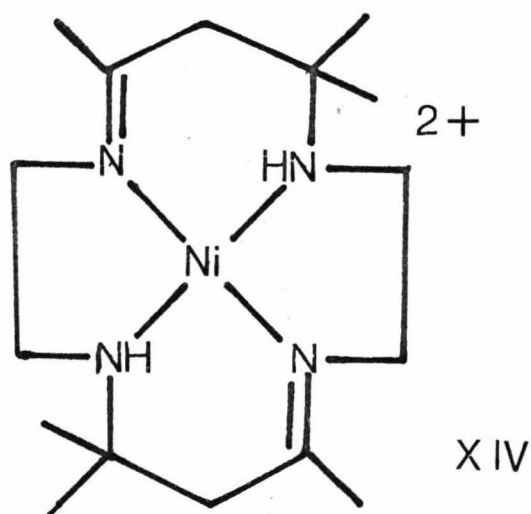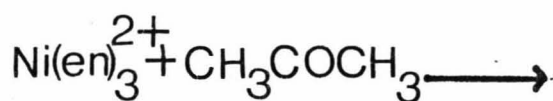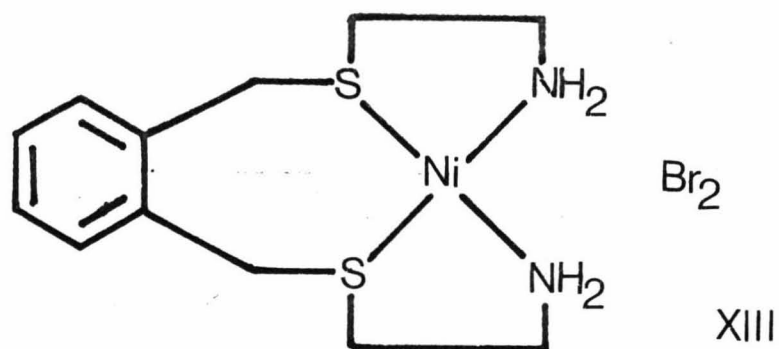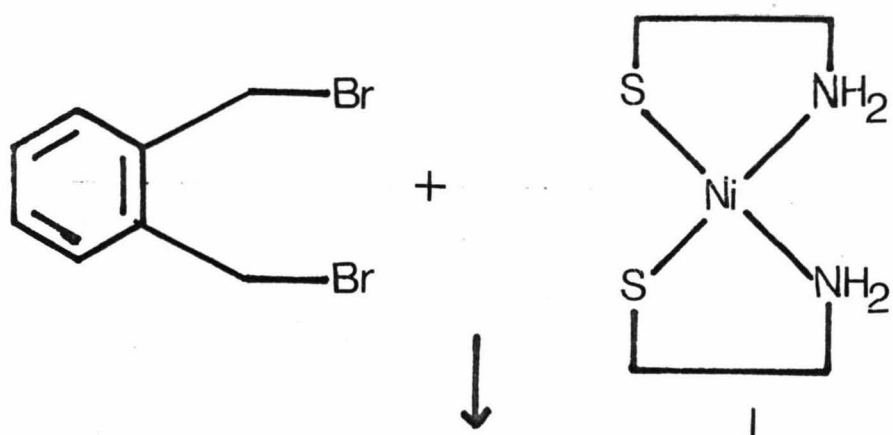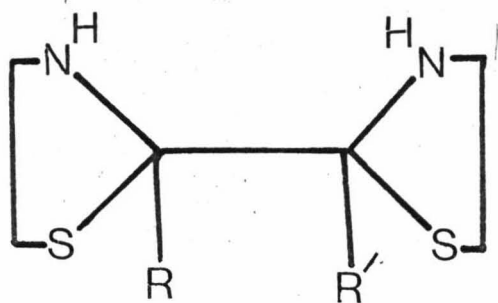
XVII

XVIII

XX

XIX

XXI

XXIV

XXV

XXXIII

$-OH$

HO

XXXIV

XXXVa

XXXVb

XXXVI

$\xrightarrow{H_2O}$

FIG.
XXXVII

$\xrightarrow{2H_2O}$

Br_2

XXXVIII