CHAPTER III
Jensen (121) has prepared a number of complexes of nickel(II) of the general formula \([\text{NiX}_2(\text{PR}_3)_2]\) (where \(R\) is Et, \(X\) is Cl, Br, I or \(\text{NO}_3\) and when \(R\) is Pr or Bu, \(X\) is Cl). Except with nickel(II) nitrate, the complexes had a dipole moment of approximately zero and were, therefore, suggested to have a trans square planar configuration. This configuration has since been confirmed by Scatturin and Turco (162) who have studied the complex \([\text{NiBr}_2(\text{PET}_3)_2]\) by X-ray diffraction method. The complex of nickel(II) nitrate with larger dipole moment of \(8.8 \times 10^{-18}\) e.s.u. was suggested to have a cis square planar structure. But the magnetic moment of 3.1 B.M. for this complex determined later by Asmussen and coworkers (3) led to the suggestion of a tetrahedral configuration which has found support from the preliminary X-ray examination of this complex by Scatturin and Turco (162). Beg and Clark (11) have isolated stable nickel(II) complexes with trimethyl phosphine and dimethyl-trifluoromethylphosphine which possess the general formulae \([\text{Me}_3\text{P}]_2\text{NiX}_2\) and \([\text{Me}_2\text{PCF}_3]_2\text{NiX}_2\) \((X\) is Cl, Br, I, SCN or \(\text{NO}_3\)) respectively. Only the complexes of nickel(II) nitrate were paramagnetic and like their triethylphosphine analogue, were assumed to be tetrahedral. Turco and Giacometti (177) have prepared a series of complexes of the type \([\text{NiX}_2.2\text{PR}_3]\)
and have investigated their visible and ultraviolet absorption spectra. Turco and coworkers (178) have obtained complexes of the type \( \text{NiX}_2(\text{PCy}_3)_2 \) (where Cy is \( C_6H_{11} \) and X is Cl, Br, or SCN). All the complexes are diamagnetic and their X-ray investigations indicate trans planar arrangement of the ligands.

Jensen (121) tried to isolate the complexes of nickel(II) with triphenylphosphine in ethanol but failed. Yamamoto and his coworkers (192) have, however, isolated the complex \( [(\text{Ph}_3\text{P})_2\text{NiBr}_2] \) by refluxing a mixture of triphenylphosphine and nickel(II) bromide in butanol. Venanzi (180) has prepared the complexes \( [(\text{Ph}_3\text{P})_2\text{NiX}_2] \) (X is Cl, Br, I or NO\(_2\)) using acetic acid as the solvent. These complexes were found to be paramagnetic with magnetic moments corresponding to two unpaired electrons. These were assigned tetrahedral structure on the basis of their conductance, dipole moment and X-ray diffraction studies. The thiocyanato analogue was found to be diamagnetic and was presumed to be trans square planar in configuration.

The complexes of the type \( \text{L}_2\text{NiX}_2 \) (where L is tri-p-tolyl phosphine or tri-p-methoxyphenylphosphine; X is Cl, Br, I, or SCN) have been reported by Venanzi and his coworkers (20). While the halogen complexes were paramagnetic and were assigned, on the basis of X-ray evidence, a pseudo-tetrahedral structure in solid state, the thiocyanato complexes were diamagnetic and were assumed to be planar. However, spectral studies of chloro and bromo
complexes in benzene solution indicated the existence of an equilibrium between the paramagnetic species and small amount of the diamagnetic species. This type of equilibrium has also been observed by Cousmaker and his coworkers (67) who have prepared and investigated the properties of complexes of the type $L_2NiX_2$ (L is $Bu_2PhP$ or $BuPh_2P$; X is Cl,Br,I,SCN or NO$_3$).

The complexes with dibutylphenylphosphine were para-magnetic and presumably tetrahedral in solid state. In benzene solution they appeared to form a mixture of diamagnetic and para-magnetic forms. The existence of this type of equilibrium has been confirmed by Venanzi and coworkers (21) who have actually separated the two isomeric forms, one paramagnetic and other diamagnetic, in case of the complexes $[(PhCH_2PPh_2)_2NiX_2]$ (X is Cl,Br or I) and $[(CH_2(CHCH_2PPh_2)_2NiBr_2]$. They have also prepared the complexes of the type $NiX_2L_2$ (X is Cl,Br,I or SCN and L is $(PhCH_2)_3P$ or $(PhCH_2)_2PPh$) all of which have been found to be monomeric, diamagnetic and consequently square planar in configuration. The thiocyanato complexes were invariably diamagnetic.

Hayter and Humiec (95) have studied the complexes of diphenylethylphosphine with nickel(II) halides. While the chloro complex was diamagnetic and thus square planar in solid state, the bromo and iodo complexes were paramagnetic and in solution they were a mixture of geometric isomers which were actually separated in case of $[(Ph_2EtP)_2NiBr_2]$. These
authors have further succeeded in isolating such geometric isomers in the case of the complexes of the type \([\text{NiX}_2(\text{PRPh}_2)_2]\) (where \(X = \text{Br, R is n-Pr, iso-Pr, n-Bu; and when X is Cl, R is n-Bu}\)). Cotton and coworkers (63) have reported the preparation and structural characterisation of the complexes containing the anions \([\text{Ph}_3\text{PNiBr}_3]^-\) and \([\text{Ph}_3\text{PNiI}_3]^-\) and also the complexes of the type \([\text{Ni(Ph}_3\text{F})_2X_2]\). Hayter and Humiec (97) have reported nickel(II)halide complexes of some diphenyl alkylphosphines (alkyl is Me, Et, iso-Pr, Bu, iso, sec- and ter-Bu and n-amyl) where eight examples of square planar-tetrahedral isomerism have been identified. Shupack (164) has studied the complex of tricyclopropylphosphine with nickel(II) chloride which has been found to be non-conducting and paramagnetic indicating tetrahedral configuration in the solid state. In the benzene solution the magnetic moment of 1.27 B.M. indicates the existence of about 61 per cent of square planar isomer.

Cass and coworkers (29) have reported a number of nickel (II) halide complexes of p-dimethylaminophenyl-dimethyl phosphine and have compared them with those formed by the unsubstituted ligand and the ligand containing p-trifluoromethylphenyl group. Chatt and Shaw (48) have prepared complexes of the type \([R'_3F)_2\text{NiRX}]\) and \([R'_3F)_2\text{NiR}_2]\) (where \(R\) is ortho substituted aryl group or an ethynyl or substituted ethynyl group). All the complexes have been
found to have a trans planar arrangement of groups around the nickel atom. Phillips and coworkers (150) have isolated complexes of the type \((\text{Et}_3\text{P})_2\text{Ni}(\text{C}_6\text{H}_5)\text{X}\) (X is Cl, I or SCN). Hayter and Humiec (96) have reported the preparation of square planar nickel mercaptide complexes of the general formulae \([\text{Ni}(\text{SC}_{6}\text{H}_5)_2\text{L}_2]\) where L is \(\text{Et}_3\text{P}\) or \(\text{PhEt}_2\text{P}\). Rick and Pruett (155) have obtained a five coordinate complex of nickel(II) having the composition \(\text{[PhP(0Et)]Ni(CN)g}\) 

Diethylphosphine reacts with nickel(II)halides to give six coordinate complexes of the type \([\text{NiX}_2(\text{Et}_2\text{PH})_4]\) (X is Cl or Br) (111). The magnetic and dipole moment data shows that these complexes are octahedral with cis-arrangement of halogen atoms. With diphenylphosphine, Issleib and Wenschuh (118) have isolated another type of complex by reacting it with anhydrous nickel(II) bromide to get the diphosphide \([\text{Ni}(\text{PPh}_2)_2(\text{PHPh}_2)_2]\). However, with dicyclohexylphosphine, Issleib and Tzschach (117) have obtained the normal four coordinate complex \([\text{NiBr}_2(\text{PHCy}_2)_2]\). Issleib and Wilde (119) have reacted phenylphosphine with nickel bromide to isolate the six coordinate complex \([\text{NiBr}_2(\text{PH}_2\text{Ph})_4]\).

Chatt and his coworkers (34,37) have reported the formation of nickel(0) complexes of the type \([\text{Ni}(\text{diphos})_2]\) (where diphos is \(\text{C}_2\text{H}_4(\text{PPh}_2)_2\) or \(\text{o-C}_6\text{H}_4(\text{PR}_2)_2\) and R is Et or Ph) by the action of the corresponding diphosphine on
nickel tetracarbonyl or directly on Raney nickel at elevated temperature. Nickel(0) complexes of the type \([\text{Ni(diphos)}]_2\) (diphos is \(\text{C}_2\text{H}_4(\text{PR}_2)_2\) and \(R\) is Me or Et) have been isolated by Chatt and coworkers (38) by the reduction of the corresponding nickel(II) complex in the presence of free ligand with sodium borohydride or sodium naphthalenide. Behrens and Mueller (13) have isolated the nickel(0) complex \([\text{Ni(DPE)}]_2\) by treating \(\text{K}_4[\text{Ni(CN)}]_4\) with 1,2-bis(diphenylphosphino)ethane in liquid ammonia. Nickelocene has been reacted with this diphosphine in cyclohexane to yield \([\text{Ni(DPE)}]_2\) (12). Horrocks and Van Hecke (179) have also prepared nickel(0) complexes \([\text{Ni(Ph}_2\text{P(CH}_3)_n\text{PPh}_2)]_2\) (where \(n\) is 2 or 3) by the reaction of the respective diphosphine with nickelocene.

Chatt and his coworkers (34,37) have reacted nickel tetracarbonyl with ditertiary phosphines like \(\text{o-C}_6\text{H}_4(\text{Pr}_2)_2\) and \(\text{C}_2\text{H}_4(\text{Pr}_2)_2\) (\(R\) is Me, Et or Ph) to isolate complexes of the type \([\text{Ni(CO)}]_2(\text{diphos})\). While aliphatic diphosphines could not replace the remaining two carbonyl groups, the treatment of this dicarbonyl complex with excess of aromatic ligands like \(\text{C}_2\text{H}_4(\text{PPh}_2)_2\), \(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2\) and \(\text{o-C}_6\text{H}_4(\text{PPh}_2)_2\) resulted in the displacement of all the carbonyl groups to give nickel(0) complexes of the type \([\text{Ni(diphos)}]_2\). Burg and Street (23,24) have treated tetracarbonyl nickel(0) with the diphosphines \((\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P( CF}_3)_2\) and \((\text{CF}_3)_2\text{PCHF_2CHF}_2\text{P( CF}_3)_2\) to get dicarbonyl complexes \([\text{Ni(diphos)(CO)}]_2\).
Stone and coworkers (137) have prepared the organo-nickel halide complexes \([\text{DPE}Ni(C\text{C}_2\text{F}_7)I]\) and \([\text{DPE}Ni(C\text{C}_2\text{F}_6)I]\) (where DPE is 1,2-bis(diphenylphosphino)ethane) by treating the diphosphine-nickel-dicarbonyl with perfluoroethyl- and perfluoro-ethyl iodide. Hayter and Humiec (96) have reacted this diphosphine-nickel-dicarbonyl with \((C\text{C}_6\text{H}_5)_2S_2\) to isolate the mercaptide complex \([\text{Ni}(SC\text{C}_6\text{H}_5)_2(\text{diphos})]\).

Hieber and Neumair (103) have reported the preparation of monomeric complex \([\text{Ni(NO)}(\text{DPE})I]\) by the reaction of 1,2-bis(diphenylphosphino)ethane on trinitrosyl nickel iodide. When this diphosphine was reacted with mononuclear phosphine complexes of nickel nitrosyl halide, they got bimnuclear complexes of the type \([\text{Ni}_2(\text{NO})_2(\text{PR}_3)_2(\text{DPE})X_2]\) (R is \(C\text{C}_6\text{H}_5\) or \(C\text{C}_6\text{H}_11\); X is Br or I). Similarly nitrosyltricyanomethanido nickel reacted with DPE to yield the complex \([\text{Ni(NO)}(\text{DPE})C(\text{CN})_3]\) (10). Hieber and Kummer (12) have studied the reaction of tetrameric nitrosyl nickel halides with tetraphenyldiphosphine and have got dimeric halogen bridged complexes of the type \([\text{Ph}_2\text{P.P.Ph}_2(\text{ON})\text{NiX}_2]\).

Wymore and Bailar (191) have obtained the nickel(III) complex \(\text{Ni(Et}_2\text{PC}_2\text{H}_4\text{PPh}_2)\text{Br}_3\) by the oxidation of the complex \([\text{Ni(diphos)}\text{Br}_2]\) with bromine. The complex is presumed to have got a polymeric octahedral structure in the solid state. Horrocks and Van Hecke (179) have also prepared nickel(III) complexes \(\text{Ni(diphos)}\text{Br}_3\) (where diphos is \(\text{Ph}_2\text{P(CH}_2)_n\text{PPh}_2\), \(n = 2\) and 3) by the oxidation of the corresponding nickel(II) complex with bromine.
Wymore and Bailor (391) have reported the preparation of 1,2-bis(dieethylphosphino)ethane and its nickel(II) complexes of the type \([\text{Ni(diphos)}X]_2\) (\(X\) is Cl or Br) and \([\text{Ni(diphos)}_2(\text{ClO}_4)_2]\). The complexes, being diamagnetic, have been presumed to be planar. Chatt and Hart (34) have reported nickel(II) complexes \([\text{NiX}_2(o-C_6H_4(\text{PET}_2)_2)]\) (\(X\) is Cl, Br or I) by the halogenation of corresponding dicarbonyl nickel(0) complexes. The reaction of bromine with the complex \([\text{Ni} (o-C_6H_4(\text{PET}_2)_2)_2]\) gave a mixture of the complexes \([\text{NiBr}_2(o-C_6H_4(\text{PET}_2)_2)]\) and \([\text{NiBr}_2(\text{diphos})_2]\). Issleib and Hohlfeld (113) have prepared a number of complexes by reacting anhydrous nickel(II) bromide with the diphosphines \(\text{Cy}_2P(\text{CH}_2)_n\text{PCy}_2\) (\(n\) is 3, 4 or 5; \(\text{Cy}\) is \(\text{C}_6\text{H}_{11}\)) in isopropyl alcohol. All the complexes with the general formula \([\text{NiBr}_2(\text{diphos})]\) were monomeric, non-electrolytes and diamagnetic with a planar arrangement of ligands. Issleib and Schwager (116) have used tetracyclohexyl diphosphine as the ligand to prepare complexes of the type \([\text{NiX}_2(\text{diphos})]\) (\(X\) is Cl or Br) in which the ligand forms three membered rings with the central metal atom. Chatt and Booth (31) have isolated nickel(II) halide complexes of the type \([\text{NiX}_2(\text{diphos})]\) (\(X\) is Cl, Br or I; the diphos is \(\text{Ph}_2\text{PCH}_2\text{PPPh}_2\), \(\text{R}_2\text{P(CH}_2)_2\text{PR}_2\) where \(\text{R}\) is \(\text{Me, Et or Ph}\)). All the complexes have a cis square planar structure. Chatt and coworkers (38) have also prepared the complexes \([\text{Ni(diphos)}_2(\text{NO}_3)_2]\) (where diphos is \(\text{C}_2\text{H}_4(\text{PPh}_2)_2\) and \(o-C_6\text{H}_4(\text{PET}_2)_2\)) by reacting nickel(II) nitrate with the corresponding diphosphine in the molar ratio of 1:2.
in acetone or alcohol. Van Hecke and Horrocks (179) have prepared and studied a number of nickel(II) complexes with the ditertiary phosphines $\text{Ph}_2\text{P(CH}_2\text{nPPh}_2$ (n is 1, 2 or 3). The complexes of the type $[\text{Ni}\{\text{Ph}_2\text{P(CH}_2\text{nPPh}_2\}\text{X}_2]$ (X is Cl, Br or I and n is 1 or 2), were diamagnetic and thus square planar. But the analogous complexes when n is 3, showed a square planar (diamagnetic)-tetrahedral (paramagnetic) equilibrium in solution.

In some cases, the bidentate ligands act more or less as monodentate. Thus Issleib and Schwager (115) have isolated the complex $[(\text{Ph}_2\text{P.P. Ph}_2)_2\text{NiBr}_2]$ in which the diphosphine acts as a monodentate ligand. The complex has been assigned a cis-square planar structure on the basis of magnetic, dipole moment and conductivity data. Chatt and Booth (31) have also reported complexes of the type $[\text{NiX}_2(\text{diphos})_2]$ (X is Cl, Br or I and diphos is $\text{Ph}_2\text{PCH}_2\text{PPPh}_2$) in which the diphosphine behaves as a monodentate ligand.

Livingstone and Lockyer (131) reacted anhydrous nickel(II) chloride and nickel(II) perchlorate with mixed bidentate ligand diphenyl(o-methylthiophenyl)phosphine (SP) to get square planar complexes $[\text{NiCl}_2(\text{SP})]$ and $[\text{Ni(SeP)}_2]$ (ClO$_4$)$_2$. Meek and his coworkers (190) have used this very ligand and its selenium analogue diphenyl (o-methylselenophenyl)phosphine (SeP) to prepare four, five and six coordinate nickel(II) complexes exemplified by the formulae $[\text{Ni(ligand)Cl}_2]$, $[\text{Ni(ligand)}_2\text{Cl]}(\text{ClO}_4)$ and $[\text{Ni(ligand)}_2\text{Cl}_2]$ respectively. The
mixed arsenic-phosphorus bidentate ligand diphenyl (o-diphenylarsinophenyl) phosphine (73) has also given similar four coordinate diamagnetic complexes \([\text{Ni}(\text{ligand})X_2]\) (X is Cl, Br, I, SCN), five coordinate diamagnetic complexes \([\text{Ni}(\text{ligand})_2X] (\text{ClO}_4)\) (X is Cl, Br, I, NO\textsubscript{2}, NCS or NCS\textsubscript{e}) and the six coordinate paramagnetic complex \([\text{Ni}(\text{ligand})_2(\text{CN})_2]\). The electronic spectra of the five coordinate complexes is indicative of square pyramidal structure instead of the usual trigonal bipyramidal structure.

Livingstone and Lockyer (131) employed the mixed tridentate ligand phenylbis(o-methylthiophenyl)phosphine (DSP) to get five coordinate chloro complex \([\text{NiCl}_2(\text{DSP})]\) and the six coordinate perchlorate complex \([\text{Ni}(\text{DSP})_2(\text{ClO}_4)_2]\). Meek and his coworkers (190), using the same tridentate ligand DSP, have isolated three types of five-coordinate nickel(II) complexes \([\text{Ni}(\text{DSP})X_2]\), \([\text{Ni}(\text{DSP})(\text{bidentate})](\text{ClO}_4)_2\) and \([\text{Ni}(\text{DSP})_2(\text{ClO}_4)_2]\). In the last complex, one of the donor atoms is probably not coordinated to the nickel atom.

Meek and his coworkers (14) have reacted the mixed tetradentate ligand tris(o-dimethylarsinopropyl)phosphine (TAP) with nickel(II) salts to get five coordinate cation \([\text{Ni}(\text{TAP})X]^+\) which has been assigned trigonal bipyramidal structure on the basis of its absorption spectra. This structure has also been confirmed by Stevenson and Dahl (175) in case of the complex \([\text{Ni}(\text{TAP})\text{CN}](\text{ClO}_4)_2\). Meek and Dyer (75)
used the mixed sulphur-phosphorus tetradentate ligand tris(o-methylthiophenyl)phosphine (TSP) to prepare trigonal bipyramidal nickel(II) complexes containing the species \([\text{Ni}(\text{TSP})X]^+\) (\(X = \text{Cl}, \text{Br}, \text{I} \) or NCS) and \([\text{Ni}(\text{TSP})L]^{2+}\) (where \(L = \text{thiourea}, \text{Ph}_3\text{P} \) or MePh\(_2\text{P}\)). The corresponding selenium-phosphorus tetradentate ligand tris(o-methylselenophenyl)phosphine (TSE) has also given similar trigonal bipyramidal nickel(II) complexes which are diamagnetic and uni-univalent electrolytes consistent with the formula \([\text{Ni}(\text{TSeP})X](\text{ClO}_4)^-\) when the fifth ligand was an anion and di-univalent electrolytes when the fifth ligand was a neutral molecule.

In the present investigation, the preparation of the complexes \([\text{Ni}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}X_2\] where \(n = 2 \) or \(4\); and \(X = \text{Cl} \) or \(\text{Br}\), has been reported. The ditertiary phosphines would be abbreviated as DPE and DPB when \(n = 2\) and \(4\) respectively.

The complexes were obtained by adding a one-molar solution of the diphosphine in hot ethanol, to a 1.1 molar solution of the respective nickel(II) halide (chloride or bromide) hexahydrate in ethanol. All the complexes separated out almost immediately and have the general formula \([\text{Ni}(\text{diphos})X_2]\) (\(X = \text{Cl} \) or \(\text{Br}\)). These are quite stable towards atmospheric moisture and can be easily handled.

DPE complexes: Both the complexes are brownish orange
<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Molar conductance in nitrobenzene (ohm·cm⁻¹)</th>
<th>Magnetic moment at 20°C (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloro 1,2-bis(diphenylphosphino)ethane-nickel(II)</td>
<td>Orange</td>
<td>2.4</td>
<td>Diamagnetic</td>
</tr>
<tr>
<td>Dibromo 1,2-bis(diphenylphosphino)ethane-nickel(II)</td>
<td>Dull orange</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Dichloro 1,4-bis(diphenylphosphino)butane-nickel(II)</td>
<td>Reddish violet</td>
<td>3.0</td>
<td>3.13</td>
</tr>
<tr>
<td>Dibromo 1,4-bis(diphenylphosphino)butane-nickel(II)</td>
<td>Green</td>
<td>1.9</td>
<td>3.15</td>
</tr>
</tbody>
</table>
in colour. As this work was in progress, the complexes with DPE were reported by Chatt and Booth (31) as well as by Van Hecke and Horrocks (179). The colour of the complexes is an indication of their square planar configuration because nickel(II) square planar complexes are frequently red, yellow or brown (66).

The conductances of millimolar solutions in nitrobenzene of these complexes were measured and it was found that they are non-electrolytes (Table III-1). Further, both of these complexes are diamagnetic which indicates square planar structure. In fact Chatt and Booth (31) have explained that the complex DPE.NiCl₂ exists in two distinct crystalline forms, dull orange needles in which the nickel has $\mu_{\text{eff}}$ value of 1.34 B.M., and the diamagnetic yellow brown plates. These observations are consistent with the square planar structure of the complexes recorded in the present work.

**DPB complexes:** The complexes of this ligand with nickel(II) have been prepared for the first time. While the complex with nickel(II) chloride is reddish violet in colour, the one with nickel(II) bromide is deep bluish green. Usually the tetrahedral nickel(II) complexes should have blue colour. The complexes under study are violet and green in colour which can be due to charge transfer absorption tailing into the visible region from the ultraviolet region. Examples of green or red
FIG: III-1

TGA CURVE FOR
DPB NiCl₂
FIG. III-2
TGA CURVE FOR DPB N:Br

WEIGHT IN M.GMS.

TEMPERATURE °C
coloured nickel(II) complexes being paramagnetic are known in literature. Thus green complexes $[\text{Ni}(\text{Pr}_3)_2X_2]$ (3) and vermilion coloured bis-1-hydroxy-acridine nickel are paramagnetic.

Both the complexes are almost non-conducting in nitrobenzene and their molar conductance is given in Table III-1. This non-conducting behaviour of the solution of the complexes is in keeping with the similar non-conducting behaviour of nickel(II) halide complexes with the ditertiary phosphines 1,1-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane and 1,3-bis(diphenylphosphino)propane (179).

The complexes were subjected to thermogravimetric analysis (TGA). The mode of decomposition of the complexes with rise in temperature is depicted in Figs.III-1 and III-2. The slight increase in weight in the initial stages indicates the air oxidation of the complex into the corresponding phosphine oxide complex. The much less increase in weight than that required for complete oxidation shows that the phosphine oxide complex is not stable at that temperature and is undergoing simultaneous decomposition. The differential thermal analysis (Fig.III-2) shows the absence of any water molecule in the complex.

Since the magnetic measurements are generally very useful in establishing the stereochemistry of nickel(II)
FIG. III-3

DATA CURVE FOR D.P.B. NiBr₂
complexes, the magnetic susceptibility of the complexes under discussion has been measured at temperatures between 85 and 294°K by Gouy's method (Tables III-2 and III-3). Paramagnetism is a definite indication of the presence of unpaired electrons whose spin and orbital angular momenta determine the magnitude of magnetic moment. In case of elements where the orbital contributions by the unpaired electrons are quenched by the bonded groups during complex formation, the magnetic moment is almost entirely dependent upon spin-angular momentum. In such cases the magnetic moment \( u_{\text{eff}} \) is given by the spin only formula

\[
\mu_{\text{eff}} = \sqrt{\frac{4S(S+1)}{3}} \text{ B.M.}
\]

where 'S' is the quantum number specifying the total spin-angular momentum of the ion. This expression is further simplified to

\[
\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}
\]

where 'n' is the number of unpaired electrons in the incomplete shell.

The electronic configurations of nickel(II) ion, in octahedral, tetrahedral and square planar environments are:

\[
\begin{align*}
\text{Ni}^{++} \text{ ion} & \quad \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\text{Ni}^{++} (\text{octahedral}) & \quad \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \times & \times \times \times \times \times
\end{align*}
\]
### Table III-2
Magnetic data of dichloro 1,4-di(diphenylphosphino)butane-nickel(II) at different temperatures

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>(T + θ)</th>
<th>X*10^6</th>
<th>X*10^6</th>
<th>H*</th>
<th>H eff</th>
<th>θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>84.5</td>
<td>96.5</td>
<td>23.47</td>
<td>84.5</td>
<td>2.839</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>93.5</td>
<td>105.5</td>
<td>21.35</td>
<td>93.5</td>
<td>2.839</td>
<td>3.03</td>
<td></td>
</tr>
<tr>
<td>102.0</td>
<td>114.0</td>
<td>19.64</td>
<td>102.0</td>
<td>2.839</td>
<td>3.04</td>
<td></td>
</tr>
<tr>
<td>120.8</td>
<td>141.8</td>
<td>15.88</td>
<td>120.8</td>
<td>2.839</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>150.5</td>
<td>162.5</td>
<td>14.02</td>
<td>150.5</td>
<td>2.839</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>180.2</td>
<td>192.2</td>
<td>11.30</td>
<td>180.2</td>
<td>2.839</td>
<td>3.11</td>
<td></td>
</tr>
<tr>
<td>236.0</td>
<td>248.0</td>
<td>8.68</td>
<td>236.0</td>
<td>2.839</td>
<td>3.13</td>
<td></td>
</tr>
<tr>
<td>293.5</td>
<td>305.5</td>
<td>6.93</td>
<td>293.5</td>
<td>2.839</td>
<td>3.20</td>
<td></td>
</tr>
</tbody>
</table>

θ = 12°K.
FIG.- III-4
INVERSE OF MOLAR SUSCEPTIBILITY AGAINST TEMPERATURE

O P B. NiCl₂
O 12° K
It can be seen that in case of square planar complex where $3d^4s^2$ orbitals are involved in the formation of covalent bonds, there are only four $3d$ orbitals available for electrons which are, thus completely paired up. The square planar complexes are, therefore, diamagnetic. In case of tetrahedral and octahedral complexes, since only the $4s^2p^3$ and $4s^2p^34d^2$ orbitals are involved respectively, the $3d$ orbitals are left with two unpaired electrons. Such complexes are paramagnetic with theoretical value of magnetic moment according to spin-only formula equal to 2.89 B.M. In practice, the paramagnetic substances have magnetic moments slightly higher than the spin-only value unless the atom is in 'S' state i.e. has no resultant orbital angular momentum. This excess called orbital increment is due to incomplete quenching of the orbital contribution to the moment.

Both the complexes under discussion are paramagnetic in behaviour with $\mu_{\text{eff}}$ equal to 3.13 and 3.15 B.M. for nickel(II) chloride and bromide complexes respectively at 20°. This paramagnetism indicates that the complexes are spin free in the solid state having two unpaired electrons. As already mentioned, nickel(II) can exist in one of the three stereochemistries, square planar, tetrahedral or octahedral. The fact that the square planar complexes are invariably
### Table III-3
Magnetic data of dibromo 1,4-bis(diphenylphosphino)butane-nickel(II) at different temperatures

<table>
<thead>
<tr>
<th>Temp. °K</th>
<th>(T + θ)</th>
<th>$\chi_0 10^6$</th>
<th>$\chi_m 10^6$</th>
<th>$\chi_m' 10^6$ (corrected)</th>
<th>$\mu_{eff} = 2.839 \chi_m'T$</th>
<th>$\mu_{eff} = 2.839 \chi_m'(T+θ)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.0</td>
<td>92.0</td>
<td>20.74</td>
<td>13380</td>
<td>13677</td>
<td>3.08</td>
<td>3.18</td>
</tr>
<tr>
<td>95.0</td>
<td>101.0</td>
<td>19.04</td>
<td>12280</td>
<td>12577</td>
<td>3.10</td>
<td>3.20</td>
</tr>
<tr>
<td>104.0</td>
<td>110.0</td>
<td>17.72</td>
<td>11430</td>
<td>11727</td>
<td>3.13</td>
<td>3.22</td>
</tr>
<tr>
<td>130.5</td>
<td>136.5</td>
<td>14.08</td>
<td>9080</td>
<td>9377</td>
<td>3.15</td>
<td>3.21</td>
</tr>
<tr>
<td>152.4</td>
<td>158.4</td>
<td>12.03</td>
<td>7764</td>
<td>8061</td>
<td>3.15</td>
<td>3.21</td>
</tr>
<tr>
<td>182.3</td>
<td>188.3</td>
<td>10.07</td>
<td>6494</td>
<td>6791</td>
<td>3.16</td>
<td>3.21</td>
</tr>
<tr>
<td>207.5</td>
<td>213.5</td>
<td>8.62</td>
<td>5561</td>
<td>5858</td>
<td>3.13</td>
<td>3.17</td>
</tr>
<tr>
<td>292.5</td>
<td>288.5</td>
<td>6.08</td>
<td>3924</td>
<td>4221</td>
<td>3.15</td>
<td>3.18</td>
</tr>
</tbody>
</table>

$\theta = 6{^\circ}K$. 
diamagnetic in the solid state, rules out the possibility of this environment around nickel in these complexes. These spin-free paramagnetic complexes are, therefore, either tetrahedral or octahedral.

In tetrahedral nickel(II), the ground term is $^3T_1$ and the magnetic moment of a complex containing $T$ ground term is calculated by summing up the first and second order Zeeman effect among the states which are originated by the splitting of the ground term under the action of spin-orbit coupling. This degeneracy of the ground term is responsible for the orbital contribution to the magnetic moment. Theoretical calculations show that a regular tetrahedral complex, containing all the four identical ligating atoms, should have magnetic moment value lying in the range 3.5-4.2 B.M. which is dependent on temperature. The octahedral nickel(II) complexes, due to the absence of orbital degeneracy, have magnetic moments within the limits 2.8 (spin only) and 3.4 B.M. Literature survey shows that the magnetic moment of the tetrahedral complexes containing the ligands, which are all identical or are close together in the spectrochemical series, are found to be in the range 3.7 - 4.0 B.M. This is consistent with the theoretical prediction. However, the tetrahedral complexes of nickel(II) with ligating atoms lying quite apart in the spectrochemical series, are reported to possess magnetic moment
values in the lower range of 2.8 - 3.4 B.M. and are independent of temperature. This is usually expected for octahedral complexes and is because of the loss of degeneracy in the ground term in the presence of ligand fields of heterogenous field strengths which give rise to magnetic moment similar to that for octahedral environment.

In the case of the complexes under discussion the two types of four ligating atoms viz. phosphorus and halogen are well separated from each other in the spectrochemical series. This suggests the absence of orbital degeneracy of the ground term and anticipates a magnetic moment value in the range 2.8 - 3.4 B.M. for tetrahedral configuration. Since the experimental values of 3.13 and 3.15 B.M. for these two complexes lie within the range of octahedral as well as tetrahedral (when the ligating atoms are well separated from each other in spectrochemical series) nickel(II) complexes, it is rather difficult to decide the stereochemistry of these two complexes simply on the basis of magnetic measurements at single temperature.

The magnetic susceptibilities for both the complexes have been measured at temperatures ranging from that of liquid nitrogen to room temperature. The reciprocal of the molar susceptibilities (after making necessary diamagnetic correction due to the ligand) are plotted against temperature. The curves which are straight lines are depicted in
Figs. III-4 and III-5. The extrapolation of these curves towards zero value of the corrected molar susceptibilities gives a θ value of 6° for DPB.NiBr₂ and 12° for DPB.NiCl₂. The magnitude of magnetic moment and its independence of temperature are in favour of octahedral structure.

Hayter and Humiec (97) have prepared and studied complexes of the type [Ni(PPh₂R)₂X₂] (R is alkyl group). The diamagnetic complexes have been assigned square planar configuration while paramagnetic ones a distorted tetrahedral structure on the basis of their reflectance spectra. While distorted tetrahedral complexes show an absorption band in the region 800-1000 μ, the square planar ones show no such bands. The square planar complexes exhibit paramagnetism in solution in which form the absorption spectra also show a band in the region 800-1000 μ which is otherwise characteristic of only tetrahedral configuration. However, the reflectance spectra of the paramagnetic complexes under study (Figs.III-6 and III-7) show absorption bands only in the region 500 and 700 μ while the bands in the region 800-1000 μ are absent. This observation is not in favour of the assignment of tetrahedral stereochemistry to these complexes and consequently the complexes are probably octahedral in nature. Even a comparison of solid state spectra of [NiBr₂(PPh₂)₂] and the complexes under study shows that the relative intensities of the two major bands in the visible region are reversed which clearly indicates that the complexes of nickel(II) investigated in this study are neither
REFLECTENCE SPECTRA OF DPB NaCl₂
tetrahedral nor square planar. So it is most likely that these complexes are distorted octahedral in the solid state and this configuration they acquire by polymerisation through halogen bridges. Butcher and coworkers (24a) have recorded the reflectance spectra of \([\text{Ni}(4-\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2)_4(\text{ClO}_4)_2]\) and absorption bands at 8000, 11700, 16300 and 27800 cm\(^{-1}\) for this distorted octahedral complex. It appears that due to high ligand field strength of diphosphines as compared to nitrogen bases, the bands at 11700 and 16300 are raised to 14000 and 20000 cm\(^{-1}\) in case of complexes under study. Since total range of visible spectra could not be recorded for these complexes, detailed assignment of bands has not been attempted.

It appears that nickel(II) halide complexes with the diphosphines 1,1-bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane have a trend from diamagnetism towards paramagnetism as the number of carbon atoms separating the two phosphorus atoms increases from one to four. When this number is one, that is, in case of the complexes with 1,1-bis(diphenylphosphino)methane (DPMe) in which the diphosphine acts as a monodentate ligand, they have purely square-planar geometry and hence diamagnetic (179). In the case of the complexes of 1,2-bis(diphenylphosphino)ethane (DPE) where the number of carbon atoms separating the phosphorus atoms is two, they are diamagnetic in the solid
Fig: V-7

Reflectance Spectra of DPB, NiBr₂

Transmittance

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state but paramagnetic in solution. The complex DPE\(_{\text{NiCl}_2}\) (31) exists in two distinct forms, one diamagnetic and the other paramagnetic. This trend continues with the complexes of 1,3-bis(diphenylphosphino)propane (DPP) which are diamagnetic as solids and paramagnetic in solution but with higher effective magnetic moment than that of DPE\(_{\text{NiCl}_2}\) (179). Presuming that this trend continues, it is to be expected that nickel(II) halide complexes of 1,4-bis(diphenylphosphino)-butane, when the number of carbon atoms separating the two phosphorus atoms is four, should be paramagnetic even in the solid state. This is borne out by the experimental values of paramagnetism as recorded above.

In respect of solubility also, there seems to be a definite trend towards decrease in solubility with increase in the number of carbon atoms separating the two phosphorus atoms in the diphosphines DPM, DPE, DPP and DPB. While complexes of DPM and DPE are freely soluble in many of the common solvents, the DPP complexes have limited solubility (179). In keeping with this trend, the DPB complexes are nearly insoluble in most of the common solvents. Due to this very low solubility of these complexes, all efforts to determine their molecular weights by cryoscopic method proved unsuccessful.
Experimental

Dichloro 1,2-bis(diphenylphosphino)ethane-nickel(II)

To a solution of DPE (2.0 g.) in hot ethanol (150 ml.)
was added a solution of nickel chloride hexahydrate (1.3 g.)
in hot ethanol (50 ml.). On shaking thoroughly, the brown-
orange complex separated out. It was filtered, washed with
hot alcohol, and dried under vacuum.

Found: Cl, 13.02, 13.11; P, 11.25, 11.33. C₂₆H₂₄P₂Cl₂Ni
requires Cl, 13.42; P, 11.73.

Molar conductance in nitrobenzene is 2.4 ohm⁻¹ cm⁻¹.

Dibromo 1,2-bis(diphenylphosphino)ethane-nickel(II)

A solution of nickel bromide hexahydrate (1.75 g.)
in ethanol (50 ml.) was added to a solution of DPE (2.0 g.)
in hot ethanol (150 ml.) with thorough shaking. The dull
orange complex separated out almost immediately. It was
filtered, washed with hot ethanol and dried under vacuum.

requires Br, 25.90; P, 10.04.

Molar conductance in nitrobenzene is 1.9 ohm⁻¹ cm⁻¹.

Dichloro 1,4-bis(diphenylphosphino)butane-nickel(II)

To a solution of DPB (2.15 g.) in hot ethanol (200 ml.)
was added a solution of nickel chloride hexahydrate (1.3 g.)
in hot ethanol (50 ml.) with thorough shaking. The solution turns reddish and soon the light reddish violet complex separated out. It was filtered, washed with hot alcohol and dried under vacuum.

Found: Cl, 12.85, 12.64; P, 10.62, 10.71. \( \text{C}_{28}\text{H}_{28}\text{P}_{2}\text{Cl}_{2}\text{Ni} \) requires Cl, 12.76; P, 11.14.

Molar conductance in nitrobenzene is 3.0 ohm\(^{-1}\)cm\(^{-1}\).

**Dibromo 1,4-bis(diphenylphosphino)butane-nickel(II)**

A solution of nickel bromide hexahydrate (1.75 g.) in hot ethanol (60 ml.) was added to a solution of DPB (2.15 g.) in hot ethanol (200 ml.). On shaking, the green complex separated out. It was cooled, filtered and washed with ethanol. It was dried under vacuum.

Found: Br, 24.90, 25.05; P, 9.23; 9.31. \( \text{C}_{28}\text{H}_{28}\text{P}_{2}\text{Br}_{2}\text{Ni} \) requires Br, 24.78; P, 9.60.

Molar conductance in nitrobenzene is 1.9 ohm\(^{-1}\)cm\(^{-1}\).