531. *Tetrahedral Nickel*(II) *Complexes and the Factors Determining Their Formation. Part II.* Complexes with Dibutylphenylphosphine and Butyldiphenylphosphine.*

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The preparation and properties of some complexes of the type L_2NiX_2 ($L = Bu^n{}_2PhP$ or Bu^nPh_2P; $X = Cl$, Br, I, SCN, or NO_3) are reported. The complexes where $L = Bu^n{}_2PhP$ and $X = Cl$, Br, or I are diamagnetic and have been assigned a *trans*-planar structure. The corresponding derivatives of Bu^nPh_2P are paramagnetic and presumably tetrahedral in the solid state, while in benzene solution they appear to form mixtures of diamagnetic and paramagnetic forms. The changes of magnetic susceptibility with changes of phosphine are discussed.

The co-ordination compounds of nickel(II) halides with trialkylphosphines have a *trans*-planar structure,[1,2] whereas those with triphenylphosphine have a tetrahedral structure.[3] Also, the complexes of trialkylphosphines are diamagnetic while those of triphenylphosphine have magnetic susceptibilities indicating the presence of two unpaired electrons, as reported in Part I.* We now report the structural and magnetic changes as a function of the number of phenyl groups attached to the phosphorus atom.

Table 1. *Colour, decomposition point, electric dipole moment, and magnetic moment of phosphine complexes of nickel*(II).

Compound	Colour	Decomp. pt.	μ (D)	$\mu_{\text{eff.}}$ (B.M.) *
$(Et_3P)_2Ni(SCN)_2$	Yellow	141—142°	—	Diamag.
$(Bu^n{}_2PhP)_2NiCl_2$	Red	56—57	1·3	Diamag.
$(Bu^n{}_2PhP)_2NiBr_2$	Dark red	70—71	1·9	Diamag.
$(Bu^n{}_2PhP)_2NiI_2$	Bronze	87—88	3·1	Diamag.
$(Bu^n{}_2PhP)_2Ni(NO_3)_2$	Green	98—99	9·8	3·16
$(Bu^n{}_2PhP)_2Ni(SCN)_2$	Orange	120—121	1·8	Diamag.
$(Bu^nPh_2P)_2NiCl_2$	Blue	149—150	3·3	3·35
$(Bu^nPh_2P)_2NiBr_2$	Green	161—162	5·9	3·30
$(Bu^nPh_2P)_2NiI_2$	Brown	134—135	6·8	3·18
$(Bu^nPh_2P)_2Ni(NO_3)_2$	Green	154—155	9·8	3·40
$(Bu^nPh_2P)_2Ni(SCN)_2$	Orange	144—145	2·0	Diamag.
$\{(Cl{\cdot}CH_2)_3P\}_2NiBr_2$	Deep red	158—159	1·5	Diamag.
$\{(Cl{\cdot}CH_2)_3P\}_2NiI_2$	Brown-black	125—126	—	Diamag.

* In the solid state.

A number of dialkylarylphosphine and diarylalkylphosphine complexes of nickel(II) have been reported but they have not been fully investigated.[1,4,5] Two main series of complexes are described in the present paper: those of dibutylphenylphosphine and those

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* Part I, *J.*, 1958, 719.

[1] Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

[2] Asmussen, *Acta Chem. Scand.*, 1955, **9** 1391; Scatturin, *J. Inorg. Nuclear Chem.*, 1958, **8**, 447.

[3] Henn, Garton, Powell, and Venanzi, unpublished work.

[4] Cass, Coates, and Hayter, *J.*, 1955, 4007.

[5] Chatt and Shaw, *J.*, 1960, 1718.

of butyldiphenylphosphine with nickel chloride, bromide, iodide, nitrate, and thiocyanate. They were prepared by adding the liquid ligand, in a nitrogen atmosphere, to a solution of nickel salt in butan-1-ol (or ethanol in the case of nickel chloride, which is insoluble in butanol). The complexes separated immediately or in a few minutes. Those which were characterized are listed in Table 1, with their properties. All of them are non-electrolytes in nitrobenzene solution.

TABLE 2. *Temperature-dependence of paramagnetic polarisations.*

Complex	$10^6\chi_M$ (uncorr.)	$10^6\chi_M$ (corr.)	Temp. (K)	$\mu_{eff.}$ (B.M.)
$(Bu_2PhP)_2NiCl_2$	−299	+95·0 *	287°	—
$(Bu_2PhP)_2NiBr_2$	−302	+112 *	287	—
$(Bu_2PhP)_2NiI_2$	−314	+132	287	—
$(Bu_2PhP)_2Ni(SCN)_2$	−402	+10·2	290	—
$(BuPh_2P)_2NiCl_2$	+4439	+4829	288	3·35
	+5877	+6265	217	
	+7640	+8028	171	
$(BuPh_2P)_2NiBr_2$	+4095	+4507	290	3·30
	+5390	+5794	223	
	+7082	+7489	171	
$(BuPh_2P)_2NiI_2$	+3914	+4350	289	3·18
	+5130	+5570	219	
	+7036	+7475	161	
$(BuPh_2P)_2Ni(SCN)_2$	−326	+78·7	290	—

* Measurements with these compounds were also carried out at lower temperatures; the value for the corrected molar susceptibility was constant in each case.

TABLE 3. *Absorption spectra* (λ *in* mμ).

	Solution		Solid	
Complex	$\lambda_{max.}$	ε	$\lambda_{max.}$	" Absorbency " *D*
$(Et_3P)_2NiCl_2$	370	14,200		
	490	450		
$(Et_3P)_2NiBr_2$	400	6200		
	542	350		
$(Et_3P)_2NiI_2$	373	4690		
	459	2900		
	610	485		
$(Bu_2PhP)_2NiCl_2$	379	11,680	360	1·48
	495	670	390—425	sh
			500	1·29
$(Bu_2PhP)_2NiBr_2$	405	8500	385	1·67
	540	576	425—450	sh
			510	1·335
$(Bu_2PhP)_2NiI_2$	370	4040	440	1·595
	463	2750	500—575	sh
	600	490	650—725	sh
			490—510	1·58
$(BuPh_2P)_2NiCl_2$	386	4560	390	1·556
	495	692	560—580	1·30
	875	35·2	900	1·245
$(BuPh_2P)_2NiBr_2$	413	5660	420	1·54
	550	476	560—580	1·30
	880	117	912	1·135
$(BuPh_2P)_2NiI_2$	320	4530	430—450	1·60
	400	3460	500—575	sh
	500—600	sh	650—750	sh
	925	374	940	1·485
$(Et_3P)_2Ni(SCN)_2$	370	11,000	340	1·295
	450—525	sh	460	1·25
$(Bu_2PhP)_2Ni(SCN)_2$	388	9550	360	1·47
	475—525	sh	450—500	sh
$(BuPh_2P)_2Ni(SCN)_2$	402	8930	380	1·50
	475—550	sh	475—525	sh

Complexes of Dibutylphenylphosphine.—These follow closely the pattern observed for the trialkylphosphine complexes. The halides and the thiocyanate are diamagnetic and monomeric. Measurements of electric dipole moments show that they are essentially *trans*-planar in solution. The observed finite moments could be attributed to small amounts of the *cis*-isomer present in solution. Small amounts of free ligand are known to catalyse *cis*–*trans*-equilibration of this type,[6] and our complexes, being fairly labile, are very likely to contain small amounts of free phosphine.

It is interesting that for these complexes, after correction for the diamagnetic contribution of the component atoms, there is a small residual paramagnetic polarization which, at least in $(Bu^n{}_2PhP)_2NiCl_2$ and $(Bu^n{}_2PhP)_2NiBr_2$, appears to be temperature-independent (see Table 2). The only paramagnetic complex isolated is the nitrato-derivative. Its structure, like that of its triethylphosphine analogue, is still unknown.

FIG. 1. *Spectra of* $(Bu^n{}_2PhP)NiX_2$ *in benzene.*

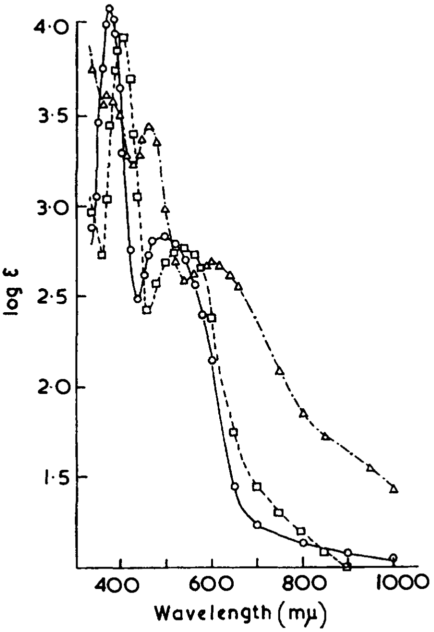
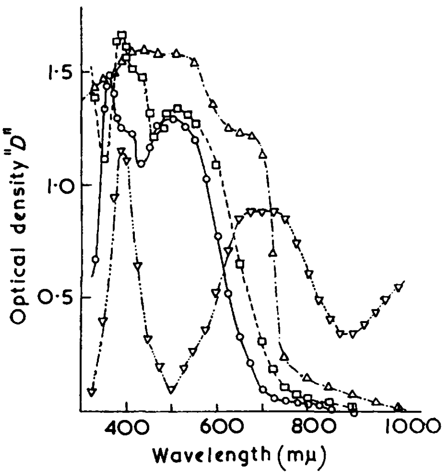


FIG. 2. *Reflection spectra of* $(Bu^n{}_2PhP)NiX_2$.



○–○ X = Cl. □–□ X = Br. △–△ X = I.
▽–▽ *Reflection spectrum of* $NiSO_4,7H_2O$.

The absorption spectra in the region 375—1000 mμ for the complexes of dibutylphenylphosphine in benzene solution are reproduced in Fig. 1. They are closely similar to those of the corresponding complexes of triethylphosphine (see Table 3). Essentially they consist of: (1) a very intense absorption band at about 400 mμ, which has been assigned to 3*d*–4*p* transitions [7] (iodo-complexes show two bands of high frequency and high intensity) and (2) the crystal-field bands in the region 500—600 mμ, which are not resolved. Our spectra are similar to those found by Giacometti and Turco [8] for other trialkylphosphine derivatives of nickel(II).

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[6] Chatt and Wilkins, *J.*, 1956, 525, and references quoted there.
[7] Williams, *J.*, 1955, 137; Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.
[8] Giacometti and Turco, *J. Inorg. Nuclear Chem.*, 1960, **15**, 242.

Attempts were made to see whether shifts of the crystal-field bands occurred on changing from benzene to a donor solvent, as observed by Chatt *et al.*[9] for complexes of platinum-(II). As our complexes were decomposed by alcohols (at a rate decreasing with increasing length of the alkyl chain of the alcohol), acetone was used: there was a slight decrease in intensity of the crystal-field bands, but no band shifts could be observed.

The reflection spectra of the solid complexes of the dialkylaryl derivatives in the region 375—1000 mμ were also recorded and these are shown in Fig. 2. The intensities are plotted on an arbitrary absorbency scale. The reflection spectrum of nickel sulphate heptahydrate, measured under similar experimental conditions, is plotted on the same graph. Our spectrum of this hydrate agrees with that reported elsewhere.[10] The major changes in spectra on passing from solution to the solid state are (1) broadening of the crystal-field bands, (2) striking decrease in intensity of the 400 mμ bands, (3) splitting of the short-wavelength bands, and (4) almost complete lack of resolution of the spectrum in the iodide complexes. There is, however, no apparent shift in the maxima of the absorption bands.

Thus, our results show that the complexes of nickel(II) with dibutylphenylphosphine are, in all respects, analogous to those with trialkylphosphines.

Complexes of Butyldiphenylphosphine.—These complexes, in contrast with those of dibutylphenylphosphine, resemble very closely those of triphenylphosphine: the only diamagnetic complex is that with nickel thiocyanate, all the others being paramagnetic in the solid state, with magnetic moments of 3·2—3·4 B.M. The temperature-dependence of the magnetic susceptibility of the solid complexes appears to follow the Curie–Weiss law over the range of temperatures investigated (160—290° K) (see Table 2). The three halogeno-complexes of this series and the thiocyanate derivative are monomeric in benzene solution, but the nitrato-complex is not sufficiently soluble in non-donor solvents to allow molecular-weight determination. The values of the electric dipole moments of the halogeno-complexes fall between those of the corresponding dibutylphenylphosphine and triphenylphosphine analogues (see Table 1 and Part I).

The visible and ultraviolet spectra of the complexes with butyldiphenylphosphine in benzene solution differ from those with dibutylphenylphosphine, the major change being the appearance of a new band at about 875—925 mμ (Fig. 3). The reflection spectra of the complexes of this series, moreover, differ from those of benzene solutions (Fig. 4): all the bands are shifted towards longer wavelengths, the crystal-field band by as much as 75 mμ. The long-wavelength bands are absent for the diamagnetic complexes of dibutylphenylphosphine, but are observed in the reflection spectra of complexes of the type $(Ph_3P)_2NiX_2$ which have tetrahedral structure in the solid state.[11]

Measurements of magnetic susceptibility of benzene solutions of the butyldiphenylphosphine halide complexes of nickel(II) were carried out by Mills and Williams,[12] who found them to have magnetic moments lower than expected for the presence of two unpaired electrons. If it is assumed that these intermediate values are due to the equilibrium:

$$\underset{\text{Diamagnetic}}{(BuPh_2P)_2NiX_2} \rightleftharpoons \underset{\text{Paramagnetic } (\mu_{\text{eff.}} = 3{\cdot}2 \text{ B.M.})}{(BuPh_2P)_2NiX_2}$$

then the amounts of the paramagnetic form present in solution can be calculated. Thus one obtains the following approximate percentages of diamagnetic form: $(BuPh_2P)_2NiCl_2$ 10%; $(BuPh_2P)_2NiBr_2$ 60%; and $(BuPh_2P)_2NiI_2$ 90%.

Two hypotheses can be put forward to explain this behaviour: (1) The diamagnetic and the paramagnetic species of the halogeno-complexes of butyldiphenylphosphine have

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[9] Chatt, Gamlen, and Orgel, *J.*, 1958, 486; 1959, 1047.

[10] Bostrup and Jörgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

[11] Davies and Venanzi, unpublished observations.

[12] Mills and Williams, personal communication.

the same structure in benzene solution. To account for the high dipole moments one has then to assume that the complexes are either *cis*-planar or distorted tetrahedral. The magnetic susceptibility of the benzene solutions could then be accounted for in terms of a diamagnetic ground state with an easily accessible paramagnetic excited state, with a multiplet separation of less than kT. (2) In benzene solution an equilibrium is set up between a *trans*-planar diamagnetic form and a tetrahedral (or *cis*-planar) paramagnetic form. Available data do not allow a definite choice but in our opinion the former is more likely.

All the thiocyanate complexes are diamagnetic and their low electric dipole moments indicate a *trans*-planar structure. In general, thiocyanates give rise to crystal field splittings larger than those due to the chloride ion,[13] and our spectral measurements are in agreement with this (see Table 3). That thiocyanate complexes of the type $(R_3P)_2Ni(SCN)_2$ are diamagnetic, irrespectively of the nature of the phosphine, may therefore be attributed to the increased crystal-field splitting induced by the thiocyanate ion.

FIG. 3. *Spectra of* $(Bu^nPh_2P)NiX_2$ *in benzene.*

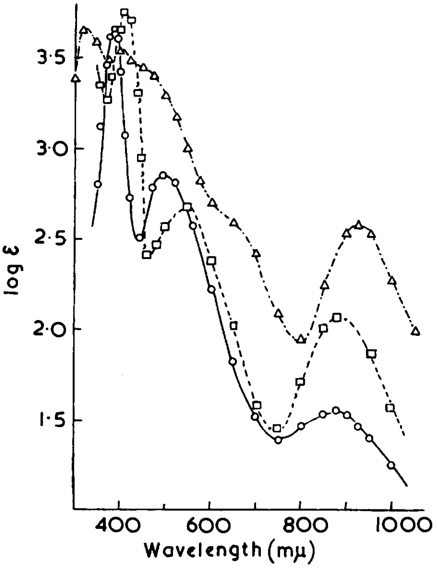
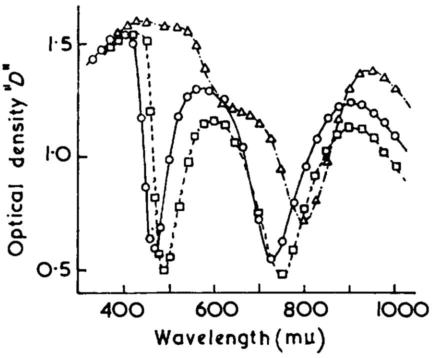


FIG. 4. *Reflection spectra of* $(Bu^nPh_2P)NiX_2$.



○–○ X = Cl. □–□ X = Br. △–△ X = I.

The contribution of the phosphines to the crystal-field splitting was shown by the thiocyanate complexes, which are the only set of compounds that is planar and diamagnetic throughout. The bands in question appear only as a shoulder at about 500 mμ, both in benzene solutions and in the solid state (see Table 3). The shifts are slight but they are towards longer wavelengths on going from Et_3P to $Bu^n{}_2PhP$ to Bu^nPh_2P, which indicates that the field becomes weaker on replacement of alkyl by phenyl groups.

For our discussion it will be assumed that the splitting between the *d*-energy levels in the square-planar complexes of nickel(II) is similar to that postulated by Chatt and Shaw [5] (see Fig. 5*b*). The spin multiplicity will be assumed to depend on the energy difference Δ between the $d_{x^2-y^2}$ and the d_{xy} energy level. If the energy difference Δ falls below a certain critical value, the increased crystal-field energy of the low-spin complex over the high-spin one may be insufficient to compensate for the loss of exchange energy which accompanies

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[13] See Mitchell and Williams, *J.*, 1960, 1912.

spin-pairing, and a paramagnetic complex will result. One could envisage this complex as preserving the square planar structure, in which the crystal-field energy might be quite small and not significantly different from that of the corresponding tetrahedral complex.[14] In the solid state the configuration of the complex will then be determined by the lattice energy, *i.e.*, by the ease of packing of the monomeric units in the unit cell. For our paramagnetic complexes the tetrahedral configuration appears to be preferred and " frozen " in the crystal lattice. In solution, however, steric repulsions between the ligands could lead to a highly distorted tetrahedral structure, with the small multiplet separation mentioned earlier.

Evidence for this hypothesis is supplied by the spectra of the halogeno-complexes of butyldiphenylphosphine both in the solid state and in solution. As mentioned earlier, the crystal-field bands are shifted by about 75 mμ towards shorter wavelength on going from the solid state to the solution (compare Figs. 3 and 4).

FIG. 5. *Proposed energy level diagram in complexes of the type* L_2NiX_2.

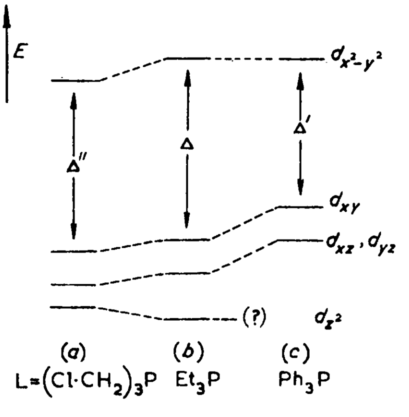
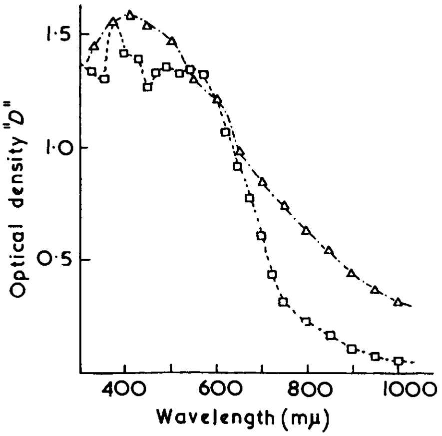


FIG. 6. *Reflection spectra of* $\{(Cl\cdot CH_2)_3P\}_2NiX_2$.



□–□ X = Br. △–△ X = I.

The gradual replacement of alkyl by phenyl groups at the phosphorus atom might be expected to weaken the crystal field generated by the ligand in two ways: (1) Inductively, by increasing the difference in electronegativity between the donor atom and the substituents. This would result in a decreased electron-donor capacity of the phosphorus atom, and consequent decrease in field strength.

(2) Mesomerically, by overlap of the π-aromatic electrons of the benzene ring (or rings) with the 3*d*-orbitals of the phosphorus atom, and consequent decrease of the π-acceptor capacity of the phosphorus atom. This, in turn, would reduce the splitting of energy levels, particularly the critical splitting of the two uppermost levels, upon which depend the magnetic properties of the complex. This relation is illustrated diagrammatically in Fig. 5c.

In an attempt to gauge the relative importance of these two factors in causing the observed structural and magnetic changes, complexes of trischloromethylphosphine, $(Cl\cdot CH_2)_3P$, were studied. Only the bromo- and iodo-complexes are reported here, as we failed to prepare the corresponding chloro-, thiocyanato-, and nitrato-derivatives. The complexes of this series are diamagnetic in the solid state. The spectra in solution could not be obtained because the compounds were either insoluble in, or decomposed by, solvents suitable for such a study. The spectra of the solids are given in Fig. 6.

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[14] Maki, *J. Chem. Phys.*, 1958, **28**, 651.

It is interesting that the crystal-field bands in these complexes occur at approximately the same wavelength as in the corresponding triethylphosphine complexes.

The inductive effect of the phenyl and chloromethyl groups can be estimated from the K_a values of phenylacetic and β-chloropropionic acid, which are $4{\cdot}88 \times 10^{-5}$ and $8{\cdot}2 \times 10^{-5}$ respectively.[15] Thus the chloromethyl group is slightly more electron-attracting (electronegative) than the phenyl group and ought therefore to decrease the crystal-field strength more than the latter group does. It follows then, on our hypothesis, that, if a change of electronegativity of the substituent at the phosphorus atom were the main factor causing the observed changes, the trischloromethylphosphine complexes should be paramagnetic, like their phenyl analogues. That this is not the case indicates that, at least in the complexes of nickel(II), d_π–d_π bonding between nickel and phosphorus is important in determining the magnetic susceptibility of the complexes, because this π-bonding appears to be significantly weakened by mesomeric interaction between the aromatic hydrocarbon radical and the phosphorus atom. The absence of such mesomeric interaction in the complexes of trischloromethylphosphine must be responsible for the diamagnetism of its nickel(II) complexes, as the electron-attracting power of the chloromethyl group would render the phosphine a poor σ-electron donor (see Fig. 5*a*).

EXPERIMENTAL

Preparation of Phosphines.—Dibutylphenylphosphine was prepared by the method of Davies and Jones [16] from dichlorophenylphosphine and butylmagnesium bromide. Butyldiphenylphosphine was prepared from butyldichlorophosphine [17] and phenylmagnesium bromide, and from chlorodiphenylphosphine and butylmagnesium bromide, the experimental conditions being similar to those used by Davies and Jones. The fraction of b. p. 120—150°/1 mm. was collected (*ca.* 70% yield) and used for the preparation of the complexes. Trischloromethylphosphine was prepared from tetrakishydroxymethylphosphonium chloride by Hoffman's method.[18] Tetrakischloromethylphosphonium chloride was recrystallized from methanol (30 c.c.) and ethyl acetate (160 c.c.), and melted at 202—203° (Hoffman gives 192—193°); when the phosphine was extracted with ether the yield was the same.

Although described as a colourless stable liquid by Hoffman, the phosphine was found to become cloudy within a few hours of preparation: this occurred on each of the four occasions on which it was prepared, despite the most rigid precautions to exclude oxygen on one occasion. Freshly prepared phosphine was used in the preparation of the complexes.

Preparations of the Complexes.—These were prepared by adding the phosphine (slightly >2 equiv.) to a solution of the nickel salt in an alcohol. Nickel chloride hexahydrate was dissolved in ethanol, and nickel bromide trihydrate and nickel nitrate hexahydrate in butan-1-ol. The solution of nickel iodide (or thiocyanate) was prepared by dissolving the stoicheiometric amount of sodium iodide (or potassium thiocyanate) in boiling butan-1-ol and adding it to a solution of nickel nitrate in butan-1-ol, filtering off the precipitate, and using the solution directly.

All preparations of the complexes were under nitrogen. In each case the complexes gradually crystallized and the mixture was cooled in ice-water before collection of the product.

The solvent used for recrystallization of the crude product, the yield of pure product, and the analytical results are tabulated for each *compound* prepared.

Analytical.—Some of the nickel analyses were carried out gravimetrically with dimethylglyoxime, and some spectrophotometrically, by measuring the absorbence of solutions of the complex produced by oxidation of bis(dimethylglyoxime)nickel(II) in the absence of ammonia.[19] The ashing of the samples before the nickel determination was done with equal volumes of concentrated nitric acid and 72% perchloric acid, refluxing for ~6 hr.

Determination of Molecular Weights.—In a previous communication it was reported that the halogeno-complexes of butyldiphenylphosphine were dimeric.[20] Subsequent investigations

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[15] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 733 *et seq.*

[16] Davies and Jones, *J.*, 1929, 33.

[17] Fox, *J. Amer. Chem. Soc.*, 1950, **72**, 4147.

[18] Hoffman, *J. Amer. Chem. Soc.*, 1930, **52**, 2995.

[19] Sandell, " Colorimetric Determination of Traces of Metals," 3rd edn., Interscience, Publ. Inc., New York, 1959, p. 668.

[20] Coussmaker, Hely-Hutchinson, Sutton, and Venanzi, International Conference on Co-ordination. Compounds, London, April 6—11th, 1959; *Chem. Soc. Special Publ.* No. 13, p. 160.

Complexes, (Phosphine)$_2$NiX$_2$.

Phosphine	X	Cryst. from [a]	Yield (%)	Found Ni (%)	Found *M*	Formula	Required Ni (%)	Required *M*
PEt_3	SCN	Me·NO$_2$	54	14·2	—	$C_{14}H_{30}N_2NiP_2S$	14·3	—
$PPhBu^n_2$	Cl	EtOH	61	10·2	570	$C_{28}H_{46}Cl_2NiP_2$	10·2	574
,,	Br	,,	53	8·9	630	$C_{28}H_{46}Br_2NiP_2$	8·85	663
,,	I	,,	62	7·8	750	$C_{28}H_{46}I_2NiP_2$	7·75	757
,,	NO_3	EtOAc–Pet	55	9·2	680	$C_{28}H_{46}N_2NiO_6P_2$	9·4	627
,,	SCN	EtOH	30	9·5	580	$C_{30}H_{46}N_2NiP_2S_2$	9·5	620
PPh_2Bu^n	Cl	Me·NO$_2$	53	9·7	[b]	$C_{32}H_{38}Cl_2NiP_2$	9·6	614
,,	Br	,,	60	8·4	[c]	$C_{32}H_{38}Br_2NiP_2$	8·35	703
,,	I	,,	32	7·5	[d]	$C_{32}H_{38}I_2NiP_2$	7·4	797
,,	NO_3	,,	27	8·9	710	$C_{32}H_{38}N_2NiO_6P_2$	8·8	660
,,	SCN	,,	54	8·8	—	$C_{34}H_{38}N_2NiP_2S_2$	8·9	—
$P(CH_2Cl)_3$	Br	[e]	42	10·2	—	$C_6H_{12}Br_2Cl_6NiP_2$	10·2	—
,,	I	[e]	54	8·5	—	$C_6H_{12}Cl_6I_2NiP_2$	8·7	—

[a] Pet = light petroleum (b. p. 40—60°). [b] 600, 589, 472. [c] 570, 648, 728, 692, 708, 690, 619. [d] 666, 781. [e] Crystallised (pure) on partial evaporation of the reaction mixture.

showed that all the complexes listed in Table 1 for which such measurements could be carried out were monomeric. These measurements were carried out cryoscopically in benzene.

Conductance Measurements.—These were done with a 10^{-3}M-solution of the complex in nitrobenzene, a Type E 7566 Mullard conductivity bridge being used. All the compounds were non-electrolytes.

Magnetic-susceptibility Measurements.—These were done (on the finely powdered solids) with a Gouy-type balance. The effective magnetic moments, $\mu_{\text{eff.}}$, were calculated from the susceptibilities at room temperature. The susceptibility values are listed in Table 2.

Absorption Spectra.—The spectra of solutions were measured at room temperature on a Beckman Ratio Recording spectrophotometer over the range 300—1000 mμ. The complete spectrum was obtained by using about 10^{-3}M-solutions for the range 700—1000 mμ, and about 10^{-4}M-solutions for the range 300—700 mμ.

The reflection spectra of the finely powdered solids were measured on a Unicam S.P. 500 spectrophotometer fitted with a Unicam diffuse reflection attachment, S.P. 540; magnesium carbonate was the reference standard.

The values of $\lambda_{\text{max.}}$ and the corresponding extinction coefficients are listed in Table 3. The intensity of absorption in the reflection spectra is given on an arbitrary scale, *D*, which varies from compound to compound.

Measurement of Electric Dipole Moments.—These were determined as described in Part I. The molar refraction R_D was evaluated from tables, the values used (in c.c.) being: Ni = 18·8;[21] C_6H_5 = 21·5, Bu^n = 19·5; SCN = 13·6; Cl = 9·1; Br = 8·9; I = 13·9; NO_3 = 9·1;[22] P = 9·1.[23]

The experimental data are listed in Table 4. The dipole moment (μ 15%) values reported were calculated after allowance for the atom polarization: $P_A = 15\%\ P_E$.

TABLE 4. *Electric dipole moments.*

(Bu$^n_2$PhP)$_2$NiCl$_2$			(Bu$^n_2$PhP)$_2$NiBr$_2$			(Bu$^n_2$PhP)$_2$NiI$_2$		
10^6w_2	ε_{12}	v_{12}	10^6w_2	ε_{12}	v_{12}	10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468	—	2·2750	1·14470	—	2·2750	1·14473
2075	2·2764	1·1443	893	2·2757	1·14446	1208	2·2773	1·14411
3702	2·2774	1·14409	1387	2·2762	1·14421	1474	2·2777	1·14404
4181	2·2778	1·14391	2129	2·2771	1·14404	2242	2·2791	1·14373
			2814	2·2778	1·14366	2797	2·2802	1·14342

(Bu$^n_2$PhP)$_2$NiCl$_2$	(Bu$^n_2$PhP)$_2$NiBr$_2$	(Bu$^n_2$PhP)$_2$NiI$_2$
$\varepsilon_{12} = 2{\cdot}2750_2 + 0{\cdot}660w_2$	$\varepsilon_{12} = 2{\cdot}2748_9 + 1{\cdot}017w_2$	$\varepsilon_{12} = 2{\cdot}2750_1 + 1{\cdot}845w_2$
$v_{12} = 1{\cdot}1446 - 0{\cdot}173w_2$	$v_{12} = 1{\cdot}1447 - 0{\cdot}362w_2$	$v_{12} = 1{\cdot}1447_1 - 0{\cdot}457w_2$
${}_TP_2$ = 238 c.c.	${}_TP_2$ = 281 c.c.	${}_TP_2$ = 418 c.c.
${}_EP_2$ = 177 c.c.	${}_EP_2$ = 183 c.c.	${}_EP_2$ = 193 c.c.
μ 15% = 1·3 ± 0·1D	μ 15% = 1·9 ± 0·15D	μ 15% = 3·1 ± 0·1D

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[21] Bentley and Sutton, *Nature*, 1932, **130**, 314.

[22] Landolt–Börnstein, " Tabellen," 1951.

[23] Jones, Davies, and Dyke, *J. Phys. Chem.*, 1933, **37**, 853.

TABLE 4. (*Continued.*)

$(\mathrm{Bu^{n}{}_{2}PhP})_{2}\mathrm{Ni(NO_{3})_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
873	2·2893	1·14440
2405	2·3158	1·14398
2932	2·3246	1·14391
3758	2·3387	1·14367

$\varepsilon_{12} = 2{\cdot}2747_9 + 17{\cdot}00w_2$
$v_{12} = 1{\cdot}14465 - 0{\cdot}264w_2$
${}_{\mathrm{T}}P_2 = 2169$ c.c.
${}_{\mathrm{E}}P_2 = 183$ c.c.
μ 15% = 9·8 ± 0·1D

$(\mathrm{Bu^{n}{}_{2}PhP})_{2}\mathrm{Ni(SCN)_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
1666	2·2766	1·14433
1834	2·2768	1·14430
2504	2·2773	1·14416
2951	2·2779	1·14398

$\varepsilon_{12} = 2{\cdot}2750_0 + 0{\cdot}961w_2$
$v_{12} = 1{\cdot}1447_0 - 0{\cdot}227w_2$
${}_{\mathrm{T}}P_2 = 281$ c.c.
${}_{\mathrm{E}}P_2 = 192$ c.c.
μ 15% = 1·8 ± 0·1D

$(\mathrm{Bu^{n}Ph_{2}P})_{2}\mathrm{NiCl_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14467
2432	2·2814	1·14363
2776	2·2821	1·14359
4077	2·2857	1·14318
5402	2·2891	1·14242

$\varepsilon_{12} = 2{\cdot}2749_8 + 2{\cdot}614w_2$
$v_{12} = 1{\cdot}1446_2 - 0{\cdot}402w_2$
${}_{\mathrm{T}}P_2 = 438$ c.c.
${}_{\mathrm{E}}P_2 = 188$ c.c.
μ 15% = 3·3 ± 0·1D

$(\mathrm{Bu^{n}Ph_{2}P})_{2}\mathrm{NiBr_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
1189	2·2822	1·14419
3065	2·2932	1·14371
4606	2·3020	1·14308
6553	2·3138	1·14218

$\varepsilon_{12} = 2{\cdot}2750_7 + 5{\cdot}895w_2$
$v_{12} = 1{\cdot}1447_1 - 0{\cdot}370w_2$
${}_{\mathrm{T}}P_2 = 941$ c.c.
${}_{\mathrm{E}}P_2 = 194$ c.c.
μ 15% = 5·9 ± 0·02D

$(\mathrm{Bu^{n}Ph_{2}P})_{2}\mathrm{NiI_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
2523	2·2920	1·14350
3805	2·3010	1·14291
4691	2·3072	1·14253
5748	2·3142	1·14218

$\varepsilon_{12} = 2{\cdot}2749_3 + 6{\cdot}844w_2$
$v_{12} = 1{\cdot}1446_4 - 0{\cdot}441_6w_2$
${}_{\mathrm{T}}P_2 = 1192$ c.c.
${}_{\mathrm{E}}P_2 = 194$ c.c.
μ 15% = 6·8 ± 0·02D

$(\mathrm{Bu^{n}Ph_{2}P})_{2}\mathrm{Ni(NO_{3})_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
384	2·2812	1·14464
419	2·2817	1·14464
463	2·2824	1·14457
484	2·2827	1·14460

$\varepsilon_{12} = 2{\cdot}2749_7 + 16{\cdot}10w_2$
$v_{12} = 1{\cdot}1446_9 - 0{\cdot}171w_2$
${}_{\mathrm{T}}P_2 = 2212$ c.c.
${}_{\mathrm{E}}P_2 = 195$ c.c.
μ 15% = 9·8 ± 0·1D

$(\mathrm{Bu^{n}Ph_{2}P})_{2}\mathrm{Ni(SCN)_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
1419	2·2767	1·14429
1828	2·2771	1·14412
2112	2·2776	1·14402
2465	2·2781	1·14384

$\varepsilon_{12} = 2{\cdot}2749_6 + 1{\cdot}238w_2$
$v_{12} = 1{\cdot}1447_1 - 0{\cdot}330w_2$
${}_{\mathrm{T}}P_2 = 313$ c.c.
${}_{\mathrm{E}}P_2 = 204$ c.c.
μ 15% = 2·0 ± 0·1D

$\{(\mathrm{Cl{\cdot}CH_{2}})_{3}\mathrm{P}\}_{2}\mathrm{NiBr_{2}}$

10^6w_2	ε_{12}	v_{12}
—	2·2750	1·14468
1198	2·2764	1·14388
1346	2·2765	1·14381
1519	2·2766	1·14357
2065	2·2771	1·14332

$\varepsilon_{12} = 2{\cdot}2750_8 + 1{\cdot}029w_2$
$v_{12} = 1{\cdot}1446_8 - 0{\cdot}672w_2$
${}_{\mathrm{T}}P_2 = 193$ c.c.
${}_{\mathrm{E}}P_2 = 118$ c.c.
μ 15% = 1·5 ± 0·2D

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