

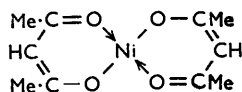
### 140. Tetrahedral Nickel(II) Complexes and the Factors Determining Their Formation. Part I. Bistriphenylphosphine Nickel(II) Compounds.

By L. M. VENANZI.

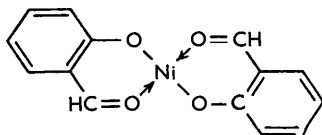
The compounds  $(\text{Ph}_3\text{P})_2\text{NiX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$ , and  $\text{SCN}$ ) have been prepared and their properties studied. The chloro- and iodo-, and presumably also the bromo- and nitrate-complexes, have tetrahedral structure, and  $\mu_{\text{eff}}$ 's of about 3 B.M. The thiocyanato-complex is diamagnetic and has *trans*-square planar structure.

The formation of tetrahedral nickel(II) complexes is discussed in terms of ligand-field theory.

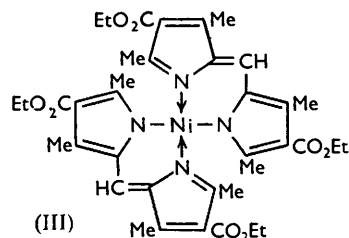
CONTRARY to general belief, tetrahedral complexes of nickel(II) are rather uncommon. This structure has been assigned to many such compounds, *e.g.*, bisacetylacetonenickel (I) ( $\mu_{\text{eff.}} = 3.2$  B.M.),<sup>1,2</sup> dehydrated bis-salicylaldehydenickel (II) (paramagnetic),<sup>3</sup> bis(diethyl-3 : 3' : 5 : 5'-tetramethylpyrromethene-4 : 4'-dicarboxylate)nickel (III) ( $\mu_{\text{eff.}} = 3.2$  B.M.),<sup>4</sup> and bistriethylphosphinedinitratonickel,  $(\text{Et}_3\text{P})_2\text{Ni}(\text{NO}_3)_2$  ( $\mu_{\text{eff.}} = 3.10$  B.M.).<sup>5</sup>



(I)



(II)



(III)

No unambiguous evidence, however, has been advanced to show that any of these is tetrahedral. Bisacetylacetonenickel is trimeric in the solid state,<sup>6</sup> and the fact that it is monomeric in pentyl benzoate<sup>7</sup> is not very significant because the latter is a donor solvent. Dehydrated bis-salicylaldehydenickel has an X-ray powder pattern different from that of bis-salicylaldehydecopper, which is said to have square planar structure,<sup>3</sup> and very similar to that of the dehydrated zinc complex, the structure of which is not known. Moreover, the nickel and the zinc complex appeared to be incompletely dehydrated.<sup>3</sup>

The pyrromethene complex (III) has been ascribed tetrahedral structure on the basis of its paramagnetism, and the fact that calculations of van der Waals radii for the molecule show serious overlap of the  $\alpha$ -methyl groups.<sup>4</sup> No molecular-weight determination, however, has been reported, and the presence of other potential donor groups in the molecule casts doubt on the validity of the conclusions.

Bistriethylphosphinedinitratonickel,  $(\text{Et}_3\text{P})_2\text{Ni}(\text{NO}_3)_2$ , has always been considered most probably to be tetrahedral. It is monomeric in benzene and has a high electric dipole moment (8.85 D).<sup>8</sup> The magnetic moment in solutions of non-donor solvents, however, has not been measured, and Nyholm has pointed out that stereochemical arrangements other than tetrahedral can also be postulated for such a compound.<sup>9,10</sup>

At the beginning of the present investigation the only well-established cases of nickel(II)

<sup>1</sup> Mellor and Craig, *J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 475.

<sup>2</sup> Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663.

<sup>3</sup> Curtiss *et al.*, *Acta Cryst.*, 1952, **5**, 388.

<sup>4</sup> Mellor and Lockwood, *J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 141.

<sup>5</sup> Asmussen *et al.*, *Acta Chem. Scand.*, 1955, **9**, 1391.

<sup>6</sup> Bullen, *Nature*, 1956, **177**, 537.

<sup>7</sup> Gach, *Sitzungsber. Akad. Wiss. Wien, Mat.-Naturwiss. Classe*, 1899, IIb, **108**, 773.

<sup>8</sup> Jensen, *Z. anorg. Chem.*, 1936, **229**, 265.

<sup>9</sup> Nyholm, *Chem. Revs.*, 1953, **53**, 263.

<sup>10</sup> Nyholm, Report to the 10th Solway Council, Brussels, 1956, 225.

ions with tetrahedral co-ordination were: (a) some sodium silicate glasses containing nickel(II),<sup>11</sup> and (b) NiCr<sub>2</sub>O<sub>4</sub>, which has a spinel structure, with the nickel atoms in the tetrahedral holes of the oxygen lattice.<sup>11a</sup>

In an attempt to isolate some tetrahedral complexes of nickel(II), the most promising set of compounds appeared to be that given by substituted tertiary phosphines.

Jensen<sup>8</sup> reported that, during the preparation of (Et<sub>3</sub>P)<sub>2</sub>Ni(NO<sub>3</sub>)<sub>2</sub>, and more markedly during the preparation of (Et<sub>2</sub>PhP)<sub>2</sub>Ni(NO<sub>3</sub>)<sub>2</sub>, a transient red colour appears, which he attributed to the formation of an intermediate square planar complex. It was therefore of interest to study the structure of the compounds of the type (Ph<sub>3</sub>P)<sub>2</sub>NiX<sub>2</sub> (X = Cl, Br, and I) described by Reppe and Schweckendiek<sup>12</sup> and by Yamamoto,<sup>13</sup> which are blue, dark green, and brown, respectively. The properties of these and two other compounds are listed in the Table.

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

Compound	Colour	Decomp. point	$\mu$ (D)	$\mu_{\text{eff}}$ (B.M.)
(Ph <sub>3</sub> P) <sub>2</sub> NiCl <sub>2</sub> .....	Blue	247—250°	—*	3.07
(Ph <sub>3</sub> P) <sub>2</sub> NiBr <sub>2</sub> .....	Dark green	222—225	5.9	2.97
(Ph <sub>3</sub> P) <sub>2</sub> NiI <sub>2</sub> .....	Brown	218—220	8.5	2.92
(Ph <sub>3</sub> P) <sub>2</sub> Ni(NO <sub>3</sub> ) <sub>2</sub> † .....	Green	224—227	—*	3.04
(Ph <sub>3</sub> P) <sub>2</sub> Ni(SCN) <sub>2</sub> † .....	Red	217—218	<3	diamag.

\* Not soluble in non-donor solvents suitable for such measurements.

† New compounds.

The bromo-, iodo-, and thiocyanato-derivatives were prepared from 2 equiv. of the phosphine and one of the nickel salt in butanol. The chloro- and nitrate-derivatives are best prepared in acetic acid.

All are non-electrolytes in nitrobenzene. Molecular-weight determinations could not be carried out owing to the high values and the low solubility in non-donor solvents. X-Ray structural work showed that solid (Ph<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> and (Ph<sub>3</sub>P)<sub>2</sub>NiI<sub>2</sub> are monomeric.<sup>14</sup> This work, which will be reported later, also shows that the chloro-complex is tetrahedral, and that the iodo-complex definitely is not *cis*-planar. This, in conjunction with dipole-moment measurements, leads to the conclusion that (Ph<sub>3</sub>P)<sub>2</sub>NiI<sub>2</sub> also is tetrahedral;<sup>9</sup> by analogy (Ph<sub>3</sub>P)<sub>2</sub>NiBr<sub>2</sub> is as well.

The thiocyanato-complex, (Ph<sub>3</sub>P)<sub>2</sub>Ni(SCN)<sub>2</sub>, because of its diamagnetism and low dipole moment, is attributed *trans*-square planar structure.

The change in stereochemistry and bond type on going from the halides to the thiocyanate is in keeping with the known empirical relation between magnetism and structure for this class of compound.<sup>1</sup>

One remarkable feature is the lability of these complexes; they are not formed in the presence of, and are decomposed by, the lower alcohols, thus explaining Jensen's failure to prepare them, and are readily decomposed by all donor solvents.

Repeated attempts to prepare the compounds (Ph<sub>3</sub>P)<sub>2</sub>NiX<sub>2</sub> (X = F, NO<sub>2</sub>, and CN) failed. Triphenylarsine and triphenylstibine also failed to form complexes, both in butanol and in acetic acid. The complexes are not formed even by tri-*p*-tolyl-, tri-*p*-anisyl-, and tri-*p*-chlorophenyl-phosphine. Failure to isolate complexes with triphenylarsine and triphenylstibine is not surprising in view of the lability of the triethylarsine complexes of nickel(II),<sup>8</sup> but it is difficult to account for the fact that *p*-substituted triphenylphosphines should not co-ordinate.

The rare occurrence of tetrahedral, paramagnetic nickel(II) complexes cannot be explained in terms of valence-bond theory. Overlap integral calculations indicate that

<sup>11</sup> Weil, Report to the 10th Solvay Council, Brussels, 1956, 419.

<sup>11a</sup> Dunitz and Orgel, *J. Phys. Chem. Solids*, 1957, **3**, 20.

<sup>12</sup> Reppe and Schweckendiek, *Annalen*, 1948, **560**, 104.

<sup>13</sup> Yamamoto, *Bull. Chem. Soc. Japan*, 1954, **27**, 501.

<sup>14</sup> Garton, Powell, and Venanzi, unpublished observations.

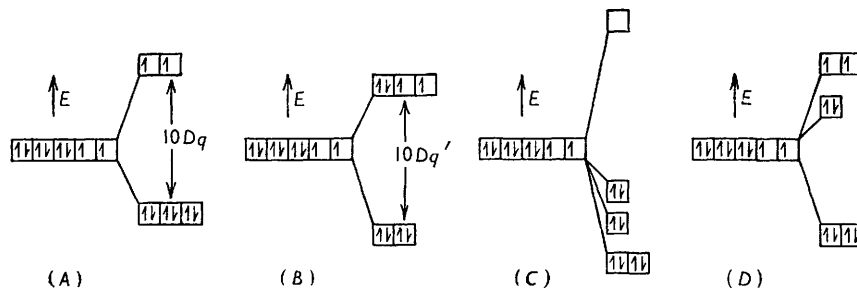
bonds involving  $4s4p^3$  or  $4s4p^34d^2$  hybridisation should be of comparable strength.<sup>15</sup> It appears, instead, that most paramagnetic nickel(II) complexes have a strong tendency to become octahedral. This is true even of the paramagnetic complexes  $[\text{NiX}_4]^{2-}$  where six-co-ordination is attained by polymerisation: *e.g.*,  $\text{K}_2[\text{NiF}_4]$ ,<sup>16</sup> which can be represented as  $\text{K}_2[\text{Ni}(\frac{1}{2}\text{F})_4\text{F}_2]$ .

A satisfactory explanation is supplied by the application of ligand-field theory to  $d^8$  systems. The splitting of the  $d$ -levels in the field generated by the ligands for various stereochemical arrangements is given in the Figure. It can be seen that in the case of a cubic (octahedral) field the crystal-field stabilisation energy is equal to  $12 Dq$ , while that for a tetrahedral field is equal to  $8 Dq'$ .<sup>17</sup> To get a rough idea of the difference in crystal-field stabilisation energy between a cubic and a tetrahedral field, let us assume that, for a given ligand, *e.g.*, ethylenediamine, the  $Dq$  values are the same for the two fields (this is probably not the case, as we shall see later, but it will be a useful initial approximation).

The  $Dq$  value<sup>17</sup> for the complex  $[\text{en}_3\text{Ni}]^{2+}$  is  $1160 \text{ cm.}^{-1}$ ; the crystal-field stabilisation energy is then  $13,920 \text{ cm.}^{-1}$ . That for the hypothetical  $[\text{en}_2\text{Ni}]^{2+}$  (tetrahedral) is then  $9640 \text{ cm.}^{-1}$ , and the difference,  $4280 \text{ cm.}^{-1}$ , corresponds to about 14 kcal.

There are no data from which to check these assumptions about  $Dq$  for tetrahedral nickel(II) complexes, and only meagre information about the values for tetrahedral complexes of other bivalent metals but, in general, it appears that, for a given ligand, the  $Dq$  values are only about one-half to two-thirds of those found in octahedral complexes.<sup>18</sup> The causes of this effect have been discussed by Orgel.<sup>19</sup>

*d-Orbital splitting due to the ligand field in  $d^8$  systems.* (A), Regular octahedral field (crystal-field stabilisation energy  $12 Dq$ ). (B), Regular tetrahedral field (crystal-field stabilisation energy  $8 Dq'$ ). (C), Square planar field. (D), Distorted tetrahedral field (Jahn-Teller effect).



Assuming that the above generalisation is valid also in the case of nickel(II) complexes, one arrives at a value of about  $500 \text{ cm.}^{-1}$  for the  $Dq$  value of the tetrahedral  $[\text{en}_2\text{Ni}]^{2+}$  ion. The crystal-field stabilisation energy would then be  $4000 \text{ cm.}^{-1}$ , and the energy difference between a cubic and a tetrahedral field about  $10,000 \text{ cm.}^{-1}$ , corresponding to about 30 kcal. It is then reasonable to assume that the energy difference between the two fields will be between 15 and 30 kcal., and this would account, to a large extent, for the rare occurrence of tetrahedral nickel(II) complexes.\*

The magnitude of the  $Dq$  values in the complexes  $(\text{Ph}_3\text{P})_2\text{NiX}_2$  is unknown, but they should not differ significantly from those calculated above.

Several authors<sup>11a,20,21</sup> have pointed out, however, that the Jahn-Teller effect will

\* Ballhausen (*Dansk Mat. Fys. Medd.*, 1954, **29**, No. 4) showed that on a simple electrostatic basis  $Dq$  (tetrahedron) =  $\frac{4}{3}Dq$  (octahedron) for complexes of the same ligand, the same interatomic distances in both fields being assumed.

<sup>15</sup> Craig *et al.*, *J.*, 1954, 332.

<sup>16</sup> Balz and Plieth, *Z. Elektrochem.*, 1955, **59**, 545.

<sup>17</sup> Orgel, Report to the 10th Solvay Council, Brussels, 1956, p. 289.

<sup>18</sup> Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

<sup>19</sup> *Idem*, *ibid.*, p. 1819.

<sup>20</sup> Jørgensen, Report to the 10th Solvay Council, Brussels, 1956, 387.

<sup>21</sup> Owen, Thesis, Oxford, 1953.

operate in tetrahedral complexes of nickel(II). Ligand-field theory predicts that in a tetrahedral field the five-fold degenerate orbital levels of the single  $d$ -electron will be split into an upper triplet and a lower doublet. The eight  $d$ -electrons of nickel(II) fill these levels in the appropriate energy order consistent with Pauli's principle and Hund's rule which gives spin  $S = 1$  (see Figure). There are then four electrons in the lower doublet and four in the upper triplet, and the energy of the system can be lowered by a Jahn-Teller distortion of the tetrahedron.<sup>11a, 20, 21</sup> This can be seen by the following argument: if the ligands are such that the tetrahedron has a two-fold axis of symmetry, a "stretching" along this axis will split the upper triplet into a lower singlet and an upper doublet, the centre of gravity of the system remaining unchanged. This splitting will be inverted if the tetrahedron is "flattened". In the case of a complex  $L_2NiX_2$  a "stretching" will reduce the  $LNiL$  and  $XNiX$  angles, and a "flattening" will increase these angles; the latter distortion will make the complex approach a square planar configuration.

With either of these distortions the energy of the seven electrons will be approximately unchanged, but that of the eighth electron will be lower if the tetrahedron is "stretched". It is therefore to be expected that the lowest energy of the system will be obtained if the tetrahedron is "stretched". This distortion, however, is not expected to be large, but it has been observed in  $NiCr_2O_4$ .<sup>11a</sup>

Asmussen *et al.*<sup>5</sup> find that  $(Et_3P)_2Ni(NO_3)_2$  has  $\mu_{eff.} = 3.10$  B.M. Nyholm,<sup>9</sup> discussing the stereochemistry and magnetism of this compound, points out that a regular tetrahedral structure would give rise to a large orbital contribution to the magnetic moment, and attributes the small magnetic moment to the perturbing effect of the asymmetric field which may cause further splitting of the triplet. This splitting need not be attributed to the asymmetric field because the Jahn-Teller effect should operate in all tetrahedral complexes of nickel(II).

The large increase in electric dipole moment from  $(Ph_3P)_2NiBr_2$  to  $(Ph_3P)_2NiI_2$  (5.9 to 8.5 D, respectively) is unexpected. Usually, in complexes *cis*- $L_2MX_2$  ( $M = Pt$  or  $Pd$ , and  $X = Cl, Br, \text{ or } I$ ) there is a slight decrease in moment from the chloride to the iodide.<sup>22</sup> This difference, however, appears to be too large to be accounted for in terms of a difference in bond angles, due to a change in magnitude of the Jahn-Teller effect with change of halogen. A full discussion of these effects will have to be postponed until bond distances and bond angles in these, and some related complexes, *e.g.*,  $(Ph_3P)_2ZnX_2$ , are known.

From the available data it appears that the transition from paramagnetic to diamagnetic complexes<sup>1, 17, 19</sup> must be attributed to the force of the field generated by the ligands, and the formation of tetrahedral compounds, instead of paramagnetic octahedral ones, will occur only when the ligands do not have enough perturbing power to cause "spin pairing" and when a tetrahedral arrangement is forced by the steric requirements of the ligands.

#### EXPERIMENTAL

*Bistriphenylphosphinedichloronickel.*—A solution of nickel chloride hexahydrate (2.38 g., 0.01 mole) in water (2 c.c.) was diluted with glacial acetic acid (50 c.c.), and triphenylphosphine (5.25 g., 0.02 mole) in glacial acetic acid (25 c.c.) added. The olive-green microcrystalline precipitate, when kept in contact with its mother-liquor for 24 hr., gave dark blue crystals which were filtered off, washed with glacial acetic acid, and dried in a vacuum desiccator ( $H_2SO_4$ : KOH); yield 84% (Found: C, 66.0; H, 4.7. Calc. for  $C_{36}H_{30}Cl_2NiP_2$ : C, 66.1; H, 4.6%).

*Bistriphenylphosphinedibromonickel.*—Triphenylphosphine (10.49 g., 0.04 mole) in boiling butanol (100 c.c.) was added to a solution of nickel bromide trihydrate (5.45 g., 0.02 mole) in boiling butanol (100 c.c.). On cooling, the pure product separated in well-formed crystals (72%) (Found: C, 58.25; H, 4.3. Calc. for  $C_{36}H_{30}Br_2NiP_2$ : C, 58.2; H, 4.1%).

*Bistriphenylphosphinedi-iodonickel.*—Nickel nitrate hexahydrate (2.91 g., 0.01 mole) in butanol (150 c.c.) was refluxed for 2 hr. with finely powdered potassium iodide (5 g., 0.03 mole). The mixture was cooled, and the solution filtered, heated to boiling, and added to a boiling

<sup>22</sup> Jensen, *Z. anorg. Chem.*, 1936, **220**, 225.

solution of triphenylphosphine (5.25 g., 0.02 mole) in butanol (50 c.c.). On slow cooling the product separated in thick plates (64%) (Found: C, 51.9; H, 3.8. Calc. for  $C_{36}H_{30}I_2NiP_2$ : C, 51.65; H, 3.6%).

*Bistriphenylphosphinedinitratonickel*.—This complex (93%) was prepared analogously to the chloro-complex (Found: C, 63.1; H, 4.5; N, 4.2.  $C_{36}H_{30}O_6N_2NiP_2$  requires C, 61.2; H, 4.3; N, 4.0%).

*Bistriphenylphosphinedithiocyanatonickel*.—This complex (76%) was prepared analogously to the iodo-complex, from nickel nitrate, potassium thiocyanate, and triphenylphosphine (Found: C, 65.4; H, 4.4; N, 3.8.  $C_{36}H_{30}N_2S_2P_2$  requires C, 64.25; H, 4.2; N, 4.0%).

*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.

*Electric Dipole-moment Measurements*.—The moments were determined by measuring the dielectric constants and specific volumes of benzene solutions at  $25^\circ$ , the small-scale technique described by Everard and Sutton<sup>23</sup> being used with the heterodyne beat capacitance meter described by Hill and Sutton.<sup>24</sup> The meter was calibrated by assuming the value 2.2727 for the dielectric constant of benzene at  $25^\circ$ .<sup>25</sup> The pycnometer was calibrated with air-free distilled water.

The dipole moments were evaluated by the method of Everard, Hill, and Sutton,<sup>26</sup> so that no allowance was made for atom polarisation except that implicit in using  $[R]_D$  as the distortion polarisation. Since the compounds are highly coloured and dissociate in strong light, it was impossible to measure the refractive index of the solutions. The molar refraction  $[R]_D$  was evaluated from tables. The values used are quoted.

Other methods of calculating the slope,  $\alpha$ , of the  $\epsilon$ - $w$  graphs, *e.g.*, that of Smith and Cleverdon,<sup>27</sup> give moments which agree with those obtained from Everard, Hill, and Sutton's method within the errors quoted. Jensen's approximate formula<sup>28</sup> was also used to evaluate the dipole moments. The values obtained will be seen to agree fairly well with those from the other methods. Differences are due to the very large values of  $P_E$  which make Jensen's assumption dubious.

Benzene of analytical grade was purified as described by Hill and Sutton.<sup>29</sup>

Atomic refraction values: phenyl = 25.8 (benzene = 26.18, H = 1.10);<sup>30</sup> P = 9.14;<sup>31</sup> Ni = 18.8  $[Ni(CO)_4 = 37.3$ ,<sup>32</sup> CO = 4.63<sup>30</sup>]; Br = 8.865; I = 13.900.<sup>30</sup>

$(Ph_3P)_2NiBr_2$						$(Ph_3P)_2NiI_2$					
$10^4w_2$	$\epsilon$	$v$	$10^4w_2$	$\epsilon$	$v$	$10^4w_2$	$\epsilon$	$v$	$10^4w_2$	$\epsilon$	$v$
0	2.2727	1.1446	4.768	2.2760	1.1443	0	2.2727	1.1446	2.577	—	1.1444
3.864	2.2754	1.1445	5.688	2.2769	1.1443	3.385	2.2764	1.1442	4.856	2.2784	1.1442
2.451	2.2745	1.1445	4.933	2.2765	1.1443	5.818	2.2794	1.1442	4.856	2.2784	1.1442
									2.587	2.2759	—

$\epsilon = 2.2727 + 7.366w_2$	$\epsilon = 2.2728 + 11.511w_2$
$v = 1.1446 - 0.589w_2$	$v = 1.1445 - 0.734w_2$
$P_T = 906.9$ c.c.	$P_T = 1710.7$ c.c.
$P_E = 205.4$ c.c.	$P_E = 215.4$ c.c.
$\mu = 5.9 \pm 0.3$ D	$\mu = 8.5 \pm 0.3$ D

Calc. from Jensen's formula :

$$\mu = 6.4 \pm 0.3 \text{ D}$$

$$\mu = 8.7 \pm 0.3 \text{ D}$$

Bistriphenylphosphinedithiocyanatonickel is probably non-polar, since its total polarisation is of the order of 200—250 c.c. and its electron polarisation should be about 210 c.c. The

<sup>23</sup> Everard and Sutton, *J.*, 1951, 16.

<sup>24</sup> Hill and Sutton, *J.*, 1953, 1482.

<sup>25</sup> Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664.

<sup>26</sup> Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

<sup>27</sup> Smith and Cleverdon, *ibid.*, 1949, **45**, 109.

<sup>28</sup> Jensen, *Acta Chem. Scand.*, 1949, **3**, 474.

<sup>29</sup> Hill and Sutton, *J.*, 1949, 746.

<sup>30</sup> Landolt-Börnstein's Tabellen, 1923, Vol. 2.

<sup>31</sup> Jones *et al.*, *J. Phys. Chem.*, 1933, **37**, 583.

<sup>32</sup> Bentley and Sutton, *Nature*, 1932, **130**, 314.

combination of low polarity and small molecular solubility made it impossible to measure the dipole moment, which is certainly less than 3 D:

$$\left. \begin{array}{l} 10^6 w_2 \\ \text{ca. } 150 \end{array} \right\} \begin{array}{l} \epsilon_{13} \\ 2.2731 \end{array} \text{ (satd. soln.)} \quad \begin{array}{l} \tau P_{\infty} = 200-250 \text{ c.c.} \\ \epsilon P_{\infty} = \text{ca. } 210 \text{ c.c.} \end{array}$$

*Magnetic-moment Measurements.*—These were done by use of a Gouy-type balance on finely powdered solids at 293° K and 90° K, and in the case of  $(\text{Ph}_3\text{P})_2\text{NiBr}_2$  and  $(\text{Ph}_3\text{P})_2\text{NiI}_2$  also at 373° K. The  $\mu_{\text{eff}}$ 's were calculated from the values of the susceptibility at 90° K.

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