

Four- and Five-Coordinate Nickel(II) Complexes with Trimethylphosphine

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The preparation of trimethylphosphine complexes of nickel halides and nickel perchlorate is reported. Stable complexes of the following types have been isolated: $[\text{NiX}_2(\text{Me}_3\text{P})_2]$, X=Cl, Br; $[\text{NiX}_2(\text{Me}_3\text{P})_3]$, X=Br, I; $[\text{NiX}(\text{Me}_3\text{P})_3]\text{ClO}_4$, X=Cl, Br; $[\text{Ni}(\text{Me}_3\text{P})_4](\text{ClO}_4)_2$. The presence of $[\text{NiCl}_2(\text{Me}_3\text{P})_3]$ in solutions of $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$ and Me_3P is indicated by visible absorption spectra measurements. The structures of the complexes, as inferred from their visible absorption spectra, magnetic moments, dipole moments, electrical conductivities and molecular weights are discussed. The four-coordinate complexes have square-planar structures, and the five-coordinate compounds presumably have *cis* trigonal-bipyramidal structures.

Whereas four-coordinate complexes of nickel(II) with ligands containing soft donor atoms such as phosphorus or arsenic have been known for several decades,¹ the tendency of nickel(II) to form five-coordinate complexes with such donor atoms has been discovered only in the last decade.² The number of known five-coordinate nickel(II) complexes has increased rapidly in the last few years, but the factors which control whether nickel(II) is coordinated in a four- or a five-coordinate manner have not yet been elucidated. A study of complexes containing only monodentate ligands should be helpful in discussing these factors because no particular configuration is demanded by such ligands.

Only a small number of well characterized five-coordinate low-spin nickel(II) complexes, containing solely monodentate ligands, have been reported. Hayter³ has prepared the halide complexes $[\text{NiX}_2(\text{HPPPh}_2)_3]$, X=Cl, Br, I, of which the bromo and iodo complexes by X-ray structure determinations⁴ have been shown to possess coordination geometries intermediate between those of trigonal-bipyramidal and square-pyramidal geometries. The ion $[\text{Ni}(\text{CN})_5]^{3-}$ has recently been isolated as a $[\text{Cr}(\text{en})_3]^{3+}$ salt which has been shown by an X-ray structure determination⁵ to contain both trigonal-bipyramidal and square-pyramidal $\text{Ni}(\text{CN})_5^{3-}$ units. Some less well characterized

nickel(II) complexes $[\text{NiX}_2\text{L}_3]$ with 2-phenyl-2-phosphaindane⁶ and 9-methyl- and 9-ethyl-9-phosphafluorene⁷ and halides as ligands have been described by Mann *et al.* Recently Turco *et al.*,⁸ Gray *et al.*,⁹ and Verkade *et al.*¹⁰ have published work on complexes of the general type $[\text{Ni}(\text{CN})_2(\text{R}_n\text{P}(\text{OR}')_{3-n})_3]$ and by physical measurements have established the presence of five-coordinate species both in the solid state and in solution. Turco *et al.*⁸ were not able to obtain five-coordinate compounds from nickel halides and tertiary phosphines. They did not, however, use trimethylphosphine in their investigations. In the case of nickel cyanide Turco *et al.*⁸ obtained five-coordinate species with a wide variety of tertiary phosphines. The peculiar role of cyanide ligands in stabilizing five-coordinate nickel(II) complexes has been discussed by Turco *et al.*⁸ who concluded that this ability may be related to a high degree of π back-bonding from the metal atom to the cyanide groups which enhances the acceptor ability of the former as well as rendering these complexes more kinetically stable than the corresponding halide complexes. This theory is supported by the fact that the anions $\text{R}-\text{C}\equiv\text{C}^-$ and CNO^- also seem to stabilize nickel(II) in a five-coordinate state.^{11,12} Finally, Verkade *et al.*¹³ have described some interesting complexes of the type $[\text{Ni}(\text{P}(\text{OR})_3)_5]\text{X}_2$, $\text{P}(\text{OR})_3=\text{P}(\text{OMe})_3$, $\text{P}(\text{OCH})_3(\text{CH}_2)_3$, and $\text{P}(\text{OCH}_2)_3\text{CR}$. These ligands have ligand field strengths comparable to CN^- and are very small, thus facilitating the uptake of a fifth ligand. The compounds presumably have trigonal-bipyramidal structures.¹³

The present paper presents the preparations and reactions of several trimethylphosphine complexes of nickel halides and nickel perchlorate. As stated in a preliminary paper,¹⁴ trimethylphosphine, unlike the higher trialkylphosphines, forms five-coordinate complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$ also when X is a halide. After this work had been completed Gray *et al.*¹⁵ described one of the complexes ($[\text{NiBr}_2(\text{Me}_3\text{P})_3]$) reported here.

Ethanol solutions of nickel halides react with trimethylphosphine to give intensely coloured solutions. In the case of nickel chloride a red 1:2 complex $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$, or a dark blue 1:3 complex $[\text{NiCl}_2(\text{Me}_3\text{P})_3]$, is formed, depending on the nickel to trimethylphosphine ratio used. The 1:3 complex, however, is only stable in the presence of excess trimethylphosphine and has not been investigated in the solid state. In contrast to nickel chloride, nickel bromide and nickel iodide readily form, respectively, dark blue and dark green 1:3 complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$, X = Br, I, which are stable in the solid state when kept under nitrogen. The corresponding 1:2 complexes could not be isolated from ethanolic solutions even when a large excess of nickel halide was used in the preparations. The red complex $[\text{NiBr}_2(\text{Me}_3\text{P})_2]$ could be obtained, however, from anhydrous nickel bromide and methylene chloride solutions of trimethylphosphine, or by refluxing the 1:3 bromo complex in such solvents as benzene or hexane. The 1:2 iodo complex could not be obtained by any of these methods. Beg and Clark¹⁶ have claimed to have prepared $[\text{NiI}_2(\text{Me}_3\text{P})_2]$ from nickel iodide and trimethylphosphine in a closed tube. Their preparation, however, could not be reproduced and the absorption maxima given by them¹⁶ for " $[\text{NiI}_2(\text{Me}_3\text{P})_2]$ " do not agree with values expected from a comparison with the spectrum of $[\text{NiI}_2(\text{Et}_3\text{P})_2]$.¹⁷ In fact, the positions given¹⁶ are close to those found in this work for the red-lilac oxidized solution of $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ (see later). The positions of the absorption maxima

Table 1. Magnetic susceptibility measurements for some trimethylphosphine nickel(II) complexes.

| Compound | 293°K | | 195°K | |
|---|-------------------|---------------------------------|-------------------|---------------------------------|
| | 10 ⁶ M | 10 ⁶ M' ^a | 10 ⁶ M | 10 ⁶ M' ^a |
| [NiCl ₂ (Me ₃ P) ₂] | -118 | 83 | -105 | 96 |
| [NiBr ₂ (Me ₃ P) ₃] | -190 | 104 | -199 | 95 |
| [NiI ₂ (Me ₃ P) ₃] | -119 | 207 | -64 | 262 |
| [NiCl(Me ₃ P) ₃](ClO ₄) | -188 | 92 | -193 | 87 |
| [Ni(Me ₃ P) ₄](ClO ₄) ₂ | -130 | 220 | -131 | 219 |

^a Corrected for diamagnetism with the Pascal constants.²¹

Table 2. Molecular weights of some trimethylphosphine nickel(II) complexes (cryoscopically in benzene solutions).

| Compound | Weight of compound, g | Weight of benzene, g | ΔT_{mp} | Molecular weight | |
|---|-----------------------|----------------------|-----------------|------------------|-------|
| | | | | found | calc. |
| [NiBr ₂ (Me ₃ P) ₃] | 0.2050 | 41.66 | 0.060 | 420 | 446.8 |
| [NiI ₂ (Me ₃ P) ₃] | 0.2750 | 22.09 | 0.121 | 525 | 540.8 |

Table 3. Absorption spectra of some trimethylphosphine nickel(II) complexes.

| Compound | Conditions | Absorption maxima, cm ⁻¹ (log ϵ) |
|---|--|---|
| [NiCl ₂ (Me ₃ P) ₂] | 2.3 × 10 ⁻³ M, (CH ₂ Cl) ₂ | 20 900 (2.58), 28 100 (4.16) ^a , 35 000 (sh, 3.1 ^b), 37 000 (3.66), 40 000 (sh, 3.8), 43 800 (4.41) ^a . |
| [NiBr ₂ (Me ₃ P) ₂] | 8.6 × 10 ⁻⁴ M, (CH ₂ Cl) ₂ | 18 700 (2.62), 26 100 (3.94), 33 300 (sh, 3.2), 36 400 (3.84), 40 800 (4.50) ^a . |
| [NiCl ₂ (Me ₃ P) ₃] | 9.7 × 10 ⁻⁴ M, (CH ₂ Cl) ₂ . | 15 200 (sh, 2.8), 17 200 (2.83), 23 500 (2.52), 29 600 (3.96), 34 500 (sh, 3.6). |
| [NiBr ₂ (Me ₃ P) ₃] | Solid | 14 500 (sh), 17 400, 23 500 (sh), 27 000 (sh), 29 000. |
| » | 1.2 × 10 ⁻³ M, (CH ₂ Cl) ₂ , 6 × 10 ⁻³ M in Me ₃ P | 14 300 (2.93), 17 100 (3.02), 23 300 (sh, 2.5), 27 800 (3.72), 34 000 (sh, 3.9), 39 500 (4.38) ^c . |
| [NiI ₂ (Me ₃ P) ₃] | Solid | 13 600, 16 900, 24 400. |
| » | 6.2 × 10 ⁻⁴ M, (CH ₂ Cl) ₂ | 13 800 (3.05), 16 700 (3.32), 25 000 (sh, 3.2), 28 600 (3.58), 35 100 (sh, 4.2), 37 500 (4.34). |
| [NiCl(Me ₃ P) ₃](ClO ₄) | Solid | 20 000, 32 500. |
| [Ni(Me ₃ P) ₄](ClO ₄) ₂ | Solid | 20 500, 31 900. |

^a 1/5 conc. ^b log ϵ -values for shoulders are the apparent values. ^c 1/2 conc.

given by Beg and Clark for $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$ do not agree either with those found in this work (Table 3).

The 1:3 complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$ are formulated as five-coordinate species for the following reasons: 1. They are diamagnetic both in the solid state (Table 1) and in solution (as shown by the sharp peaks in their ^1H NMR spectra recorded in CDCl_3). 2. They are monomeric and only slightly dissociated in freezing benzene (Table 2). 3. The molar conductivities in nitrobenzene¹⁴ are negligible. 4. The absorption spectra in ethylene chloride solution are very different from the spectra usually obtained in the visible region for square-planar nickel(II) complexes (Table 3 and Fig. 1). 5. The reflectance spectra are similar to the solution spectra (Table 3 and Fig. 2), confirming the presence of the same coordination geometries in the solid state and in ethylene chloride solutions.

As found for similar five-coordinate species^{8,10} the complexes reported here are dissociative unstable in solution, giving trimethylphosphine and the square-planar species (eqn. 1). The presence of isosbestic points in the visible

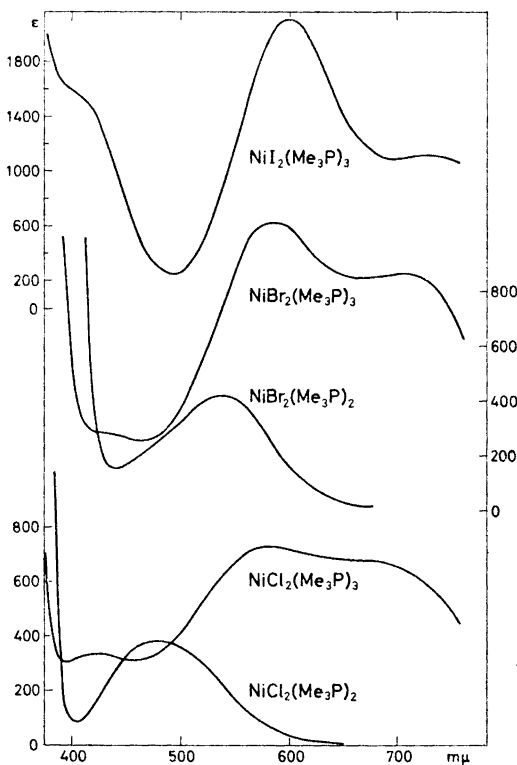
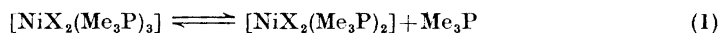


Fig. 1. Visible absorption spectra of some trimethylphosphine nickel(II) complexes.

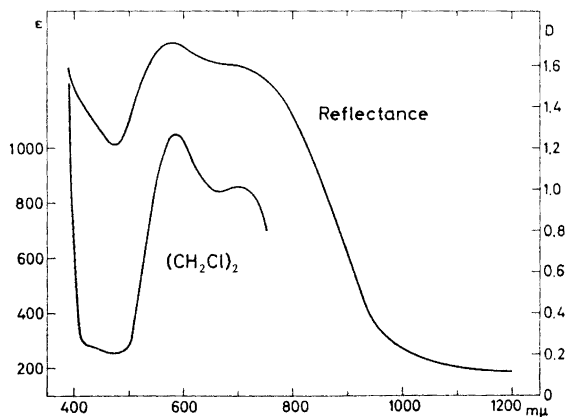


Fig. 2. Visible reflectance and solution spectra of $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$.

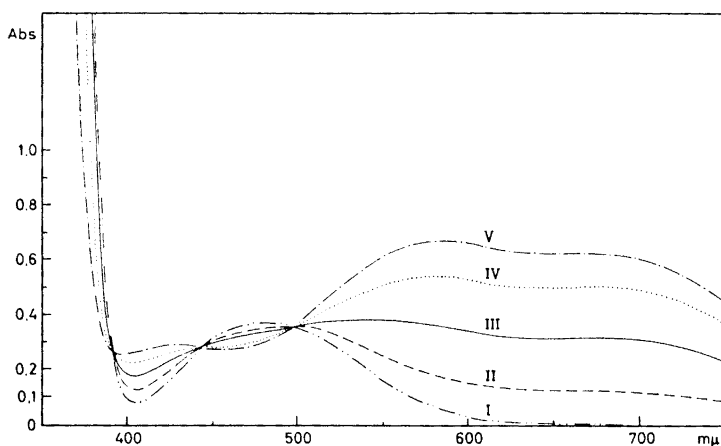


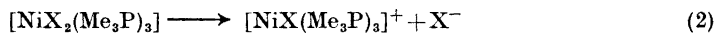
Fig. 3. Visible absorption spectra of $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$ with increasing amounts of trimethylphosphine in ethylene chloride solutions. I: Pure $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$; II: 1 mol excess; III: 6 mol excess; IV: 20 mol excess; V: 70 mol excess of Me_3P .

spectra of ethylene chloride solutions of $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$ containing increasing amounts of trimethylphosphine (Fig. 3) confirms the presence of only two species absorbing in this region. It was not possible, however, to reach constant ϵ -values for the 1:3 chloro complex even when a 100-fold excess of trimethylphosphine was added. The ϵ -values given in Table 3 for the 1:3 chloro complex are therefore only the lower limits of the "true" values. A dissociation was also observed for the 1:3 bromo complex, but in this case a 5-fold excess of trimethylphosphine was sufficient to enable constant ϵ -values to be reached. The absorption maxima and ϵ -values found in this work (Table 3) deviate

from those given by Gray *et al.*¹⁵ for $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$, especially in the UV region. The reason may be that Gray *et al.* did not take into account the dissociation of the complex according to eqn. 1. Thus, the absorption maxima above $25\,000\text{ cm}^{-1}$ given for $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$ ¹⁵ agree better with the maxima found in this work for $[\text{NiBr}_2(\text{Me}_3\text{P})_2]$ than for $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$. Finally, the spectrum of the 1:3 iodo complex in ethylene chloride was practically unaffected by the addition of trimethylphosphine, showing the degree of dissociation, (eqn. 1), to be very small in this case. The solution, however, smelled of phosphine, so a small degree of dissociation is obvious. The increased stability of the five-coordinate species, when going from Cl to I, has also been found by Hayter³ for the analogous complexes $[\text{NiX}_2(\text{HPPh}_2)_3]$, but in terms of this dissociation the trimethylphosphine complexes are much more stable in solution.

Studies of solutions of the trimethylphosphine complexes are complicated, however, by their ready oxidation by oxygen. Whereas solid $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ is stable for some hours in dry air, solutions of this complex in ethylene chloride, benzene or ethanol are oxidized within a few minutes when kept in contact with air. The oxidation is accompanied by a colour change from dark green to dark red-lilac. The colour change is accelerated when pure oxygen is bubbled through the solution, but does not occur when deaerated solvents are used and the solutions are kept under nitrogen. The absence of new infrared absorptions in the $1100\text{--}1200\text{ cm}^{-1}$ region indicates that no trimethylphosphine oxide is formed during the oxidation. The most significant change in the visible absorption spectrum is the disappearance of the band at $16\,700\text{ cm}^{-1}$ and the appearance of a more intense band at *ca.* $17\,500\text{ cm}^{-1}$ (ϵ *ca.* 4500). The 1:3 bromo complex behaves similarly even though it shows greater resistance to oxidation. The oxidation in this case is accompanied by a colour change from deep blue to deep red. The complexes formed by the oxidations are most likely nickel(III) complexes, but further examinations of the reactions and the structures of the compounds formed are postponed for a later study.

The dissociation of the five-coordinate complexes may take an alternative route in solvents which are more capable of solvating ions than are ethylene chloride or benzene. Thus, 10^{-3} M ethanolic solutions of $[\text{NiX}_2(\text{Me}_3\text{P})_3]$ have electrical conductivities corresponding to *ca.* half of the values expected for 1:1 electrolytes.¹⁴ The dissociation in this solvent, therefore, must occur by loss of a halide ion (eqn. 2). A competitive dissociation, following eqn. 1,

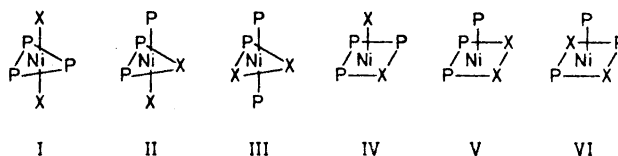


presumably also takes place in ethanol, as the intensity of the visible bands due to the undissociated bromo complex was increased in ethanolic solution by the addition of trimethylphosphine. In accordance with eqn. 2 is the fact that excess LiClO_4 added to ethanolic solutions of $[\text{NiX}_2(\text{Me}_3\text{P})_3]$, $\text{X}=\text{Cl}, \text{Br}$, changed the colour of the dark blue solutions to deep red, and complexes with the composition $[\text{NiX}(\text{Me}_3\text{P})_3]\text{ClO}_4$ could be isolated. For $\text{X}=\text{I}$ no perchlorate was precipitated presumably because the low solubility of $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ gives rise to too low a concentration of $[\text{NiI}(\text{Me}_3\text{P})_3]^+$ for precipitation to occur. The complexes $[\text{NiX}(\text{Me}_3\text{P})_3]\text{ClO}_4$ are 1:1 electrolytes in nitrobenzene,¹⁴

and are diamagnetic (Table 1). Their visible reflectance spectra show only one absorption band at *ca.* 20 000 cm^{-1} (Table 3). From this evidence a square-planar structure is inferred.

In a paper by Jensen *et al.*,¹⁸ where the difference in behaviour between trimethylphosphine and other trialkylphosphines towards nickel(II) salts was first recognised, the bromo complex was tentatively formulated as "probably a mixture of $[\text{NiBr}_2(\text{Me}_3\text{P})_2]$ and $[\text{NiBr}_2(\text{Me}_3\text{P})_4]$ ". A 1:1 mixture of such complexes, which is consistent with the analytical figures, seems to be excluded by the present evidence, *i.e.* the diamagnetism of the isolated blue complex, and the similarity of the bromo and iodo compounds, where no 1:2 complex could be obtained at all in the latter case. Also, the tentative formulation of complexes which contain coordinated ethanol to account for the conductivity of the ethanolic solutions¹⁸ is at variance with the isolation, reported here, of the unsolvated complexes $[\text{NiX}(\text{Me}_3\text{P})_3]\text{ClO}_4$ from such solutions.

The five-coordinate complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$, X = Cl, Br, I, probably have approximately the same coordination geometries, because the absorption spectra are all very alike (Fig. 1). For a NiX_2P_3 complex the ligand arrangement of highest possible symmetry is a trigonal bipyramid, I, with the two halide atoms on the C_3 axis (D_{3h} symmetry). The compounds $[\text{Ni}(\text{CN})_2(\text{R}_n\text{P}(\text{OR}')_{3-n})_3]$ prepared by Turco *et al.*,⁸ Gray *et al.*,⁹ and Verkade *et al.*¹⁰ presumably have this structure, because only one CN stretching frequency is found in the infrared spectra.⁸⁻¹⁰ For the trimethylphosphine complexes, however, the structure I is not feasible for two reasons. Firstly,



only one " $d-d$ " transition ($e' \rightarrow a'$) is symmetry-allowed in complexes with D_{3h} symmetry,¹⁹ in contrast to the three absorption bands found in the visible region of the spectra reported here (Fig. 1). Secondly, a complex with D_{3h} symmetry would have a zero electrical dipole moment, but the 1:3 bromo

Table 4. Electric dipole moments of some trimethylphosphine nickel(II) complexes (20°C in benzene solutions).

| Compound | $10^3 x$ | P^a | P_E (calc.) | $P_A + P_O$ | P_O | μ (D) |
|--|----------|-------|---------------|-------------|-------|-----------|
| $[\text{NiCl}_2(\text{Me}_3\text{P})_2]$ | 1.95 | 108 | 83 | 25 | 0 | 0 |
| $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$ | 1.39 | 931 | 115 | 816 | 786 | 6.1 |
| $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ | 1.24 | 927 | 125 | 802 | 772 | 6.1 |

^a The symbols are the ones used by Jensen *et al.*¹⁸

and iodo complexes have dipole moments in benzene solutions of the order of 6 D (Table 4). A distortion of the complexes in benzene solution, responsible for these rather large dipole moments, is at variance with the observed similarity between the absorption spectra in benzene, ethylene chloride, and in the solid state. Gray *et al.*¹⁵ have used a D_{3h} model (structure I) as a basis for discussing the spectrum of $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$ and favour interpreting the large splitting of the lowest energy absorption band in terms of a distortion of the excited state, rather than of the ground state. A distortion of the ground state, which is also considered as a possibility by Gray *et al.*, seems more likely from the dipole moment evidence presented here.

Several structures, *viz.* II–VI, should give rise to non-zero dipole moments in agreement with experiment. The complexes, however, may well have structures which are best described as intermediate between these idealized geometries. Only small distortions are necessary for the interconversion of several of the structures I–VI, and it is possible that the relative positions of the ligands in any particular complex are determined by minor differences in steric crowding or in the electrical repulsion forces between the ligands.²⁰

If it is assumed, however, that the structures of the 1:3 complexes can be approximated by one of the idealized structures II–VI, then several arguments can be formulated (based on the relative intensities and positions of the visible bands in the spectra of these complexes) which indicate that the *cis* trigonal-bipyramidal structures II or III are the most likely possibilities.

Firstly since trigonal-bipyramidal complexes usually exhibit an intense band at high wavelengths^{9,20} several five-coordinate complexes which have their most intense bands in the lower wavelength region of the visible spectrum are believed to have square-pyramidal structures.^{21,22} The present complexes exhibit intense high-wavelength bands and accordingly should belong to the bipyramidal class.

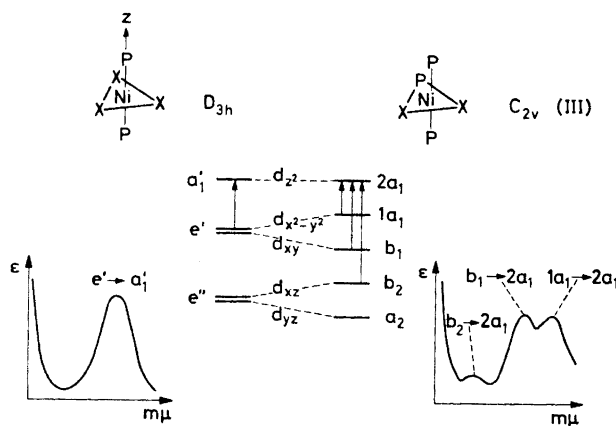


Fig. 4.

Secondly, symmetry considerations may be used to show that a complex with a trigonal-bipyramidal structure is expected to exhibit a spectrum similar to those observed experimentally. The ligand field d orbital splitting scheme for a complex with the structure III, *i.e.* C_{2v} symmetry, is shown in Fig. 4 along with the splitting scheme for a related hypothetical complex of D_{3h} symmetry. The selection rules for one-electron transitions predict one dipole-allowed transition ($e' \rightarrow a_1'$) in D_{3h} symmetry and three dipole-allowed transitions ($1a_1 \rightarrow 2a_1$, $b_1 \rightarrow 2a_1$ and $b_2 \rightarrow 2a_1$) in C_{2v} symmetry. If in the actual complexes the deviation from D_{3h} symmetry of the coordination environment of the nickel atom is not too great then the ϵ -values for the bands due to the allowed transitions in D_{3h} symmetry ($1a_1 \rightarrow 2a_1$ and $b_1 \rightarrow 2a_1$) should be larger than the ϵ -value for the band due to the transition which is dipole-forbidden in D_{3h} symmetry ($b_2 \rightarrow 2a_1$). The spectrum predicted for a C_{2v} structure from these intensity considerations (Fig. 4) is in agreement with those obtained experimentally (Fig. 1). A complex with the structure II (C_s symmetry) is also expected to give a spectrum similar to the one predicted for III, the only difference being that two less intense bands should occur at higher wavenumbers instead of one as for the C_{2v} structure. One of these weak bands, of course, could be hidden under the strong charge-transfer band which occurs at *ca.* $27\,000\text{ cm}^{-1}$, and at present there is no reason to favour one of these structures as the more probable. The spectra of the square-pyramidal cases IV–VI can also be predicted by similar considerations of the d -level ligand field splitting in these structures. The spectrum predicted for the C_{2v} case (VI) is given in Fig. 5. Here, however, in contrast to the experimental spectra, the low-intensity band(-s) is expected to lie at lower energy than the high-intensity bands.

The above treatment is no doubt an oversimplification, but a similar treatment has been used with success on several five-coordinate complexes by Venanzi *et al.*¹⁹ The structures of the five-coordinate complexes can, however,

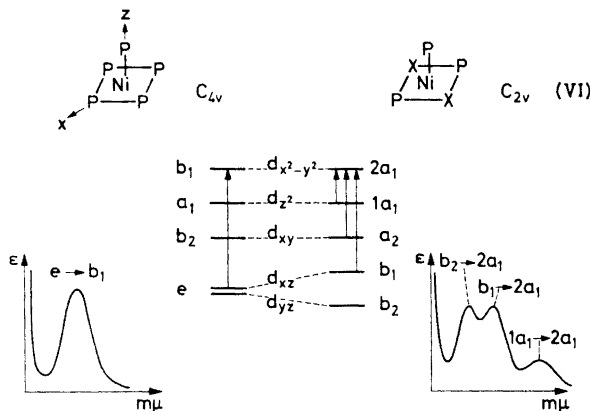


Fig. 5.

only be assigned conclusively by X-ray structure analyses. X-Ray structure investigations of the complexes $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$ and $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ are in progress and will be published shortly.²³

Finally, the reaction of trimethylphosphine with nickel perchlorate has been investigated. In contrast to the behaviour of trimethylphosphite, which forms $[\text{Ni}(\text{P}(\text{OMe})_3)_5](\text{ClO}_4)_2$,¹³ only the red complex $[\text{Ni}(\text{Me}_3\text{P})_4](\text{ClO}_4)_2$ was obtained, and no further reaction between trimethylphosphine and the complex in acetonitrile solution, or in ethanol or acetone suspensions, was observed. $[\text{Ni}(\text{Me}_3\text{P})_4](\text{ClO}_4)_2$ is diamagnetic in the solid state (Table 1) and a 2:1 electrolyte in nitrobenzene solution.¹⁴ The reflectance spectrum (Table 3), as well as the other physical measurements, agree with those expected for a square-planar structure. The complex is rather unstable in solution (it is soluble only in such polar solvents as water, nitromethane, and acetonitrile) and reliable solution spectra could not be obtained.

The behaviour of trimethylphosphine towards nickel salts, when compared with the behaviour of other trialkylphosphines, clearly demonstrates the important role of steric hindrance in determining the coordination number of nickel(II). The difference between the reactions of EtPh_2P and 9-ethyl-9-phosphafluorene with nickel halides⁷ is also compatible with the difference in steric requirements of these two ligands. However, as is illustrated by the difference between CN^- and NCS^- , where the latter forms exclusively square-planar complexes $[\text{Ni}(\text{NCS})_2(\text{R}_3\text{P})_2]$,^{8,14} factors other than steric ones must also be important. The high stability of the five-coordinate complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$ only when $\text{X} = \text{CN}^-$, Br^- , I^- and, to a smaller degree, Cl^- , seems confusing. The stabilities do not parallel either the π -acceptor properties (the halides are not π -acceptors), or the ligand field strengths in square-planar complexes, $\text{CN}^- > \text{NCS}^- > \text{R}_3\text{P} > \text{Cl}^- > \text{Br}^- > \text{I}^-$. The relative stabilities of five-coordinate versus four-coordinate nickel complexes may, however, be related to both properties. Thus, since more d -orbitals are available for π -bonding in trigonal-bipyramidal than in square-planar coordination geometries,⁹ strong π -acceptor ligands such as CN^- may stabilize a trigonal-bipyramidal structure relative to a square-planar one. On the other hand, the ligand field strengths and therefore the stabilizing powers of Cl, Br, and I decrease from Cl to I in the square-planar complexes, whilst the ligand field strengths of the halides in the complexes $[\text{NiX}_2(\text{Me}_3\text{P})_3]$ seem to be nearly equal (Fig. 1). As found in this work and in the work of Hayter³ and Mann^{6,7} this effect may stabilize the trigonal-bipyramidal complexes relative to the square-planar ones when $\text{X} = \text{Br}$ and I and when the steric hindrance between the phosphines in the complex is small.

EXPERIMENTAL

The analyses were carried out in the microanalysis department of this laboratory. The magnetic susceptibilities were measured on ca. 0.3 g samples using the Gouy method and were found to be independent of the field strength. The solution absorption spectra (13 300–45 500 cm^{-1}) were obtained on a Perkin-Elmer model 137 UV ultraviolet-visible spectrophotometer. The solvent (reagent grade ethylene chloride) was dried and deaerated before use. The reflectance spectra (8000–34 000 cm^{-1}) were obtained on a Beckman DU

Spectrophotometer model G 2400 equipped with a Beckman 2580 reflectance attachment. The infrared spectra were obtained on a Perkin-Elmer model 337 grating infrared spectrophotometer. Trimethylphosphine was prepared *via* its 1:1 silver iodide complex.^{18,25} The preparations of the nickel complexes and the physical measurements were performed under nitrogen. The melting points (uncorrected) were determined in closed tubes.

Dichlorobis(trimethylphosphine)nickel(II). Trimethylphosphine (0.38 g, 5×10^{-3} mol) was added to a solution of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ (1.20 g, 5×10^{-3} mol) in abs. ethanol (8 ml). The mixture was heated gently in order to dissolve any crystals which formed instantly, and the red solution was cooled in an ice-salt bath. The red crystals which deposited were filtered off, washed with abs. ethanol and dried *in vacuo*. Yield 0.43 g (60 %) of red crystals, m.p. 199–200°C. (Found: C 25.87; H 6.41; Cl 25.32. Calc. for $\text{C}_6\text{H}_{18}\text{Cl}_2\text{NiP}_2$: C 25.57; H 6.44; Cl 25.16). The compound was usually isolated pure, but impure samples could be recrystallized from ethanol.

Dibromobis(trimethylphosphine)nickel(II). A solution of trimethylphosphine (0.38 g, 5×10^{-3} mol) in methylene chloride (10 ml) was shaken with NiBr_2 (1.10 g, 5×10^{-3} mol) for 1/2 h and then filtered. The dark red filtrate was evaporated to a small volume and pentane was then carefully added until crystallization began. Cooling to -20°C afforded red-black crystals, which were collected on a filter and dried *in vacuo*. Yield 0.46 g (50 %), m.p. 175–180°C. (Found: C 18.74; H 4.79; Br 43.10. Calc. for $\text{C}_6\text{H}_{18}\text{Br}_2\text{NiP}_2$: C 19.45; H 4.89; Br 43.11).

The complex could be obtained also from the 1:3 complex. Thus, dibromotris(trimethylphosphine)nickel(II) was dissolved in dry benzene and the solvent was removed by distillation at the boiling point. The red powder obtained was recrystallized from pentane to give dark red crystals, m.p. 178–181°C. (Found: C 19.52; H 4.66; Br 42.19). The complex is very soluble in methylene chloride, acetone, and benzene and less soluble in pentane giving red solutions. The complex dissolves in methanol and ethanol to give blue coloured solutions. The colour and the absorption spectrum indicated the formation of dibromotris(trimethylphosphine)nickel(II), and only the 1:3 complex could be isolated by cooling these blue solutions.

Reaction of solid nickel iodide with trimethylphosphine. Powdered NiI_2 (0.316 g, 10^{-3} mol) was shaken with trimethylphosphine (0.115 g, 1.6×10^{-3} mol) in a closed tube for one week. The violet crystals obtained when treated with methylene chloride gave a dark green solution and a brown residue. The solution was evaporated to give violet-black crystals of $[\text{NiI}_2(\text{Me}_3\text{P})_3]$ (0.250 g, 98 % based on trimethylphosphine), identified by its visible absorption spectrum and by iodide titration. The residue (0.170 g) was shown by IR spectroscopy to contain no trimethylphosphine.

Dibromotris(trimethylphosphine)nickel(II). Trimethylphosphine (2.28 g, 3×10^{-2} mol) was added to a solution of $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ (2.73 g, 10^{-2} mol) in abs. ethanol (9 ml). The mixture was heated gently until a clear blue-black solution was obtained. Cooling to 0°C afforded blue-black crystals which were filtered off, washed with a small volume of cold ethanol and dried *in vacuo*. Yield 3.10 g (70 %). Recrystallization from abs. ethanol gave the pure compound, m.p. 140–150°C (decomp.). (Found: C 23.89; H 6.14; Br 35.94. Calc. for $\text{C}_9\text{H}_{27}\text{Br}_2\text{NiP}_3$: C 24.19; H 6.09; Br 35.76). The compound is very soluble in ethanol, methylene chloride, and acetone, fairly soluble in benzene and sparingly soluble in pentane giving blue solutions. Recrystallization from benzene or toluene afforded compounds containing solvents of crystallization (1/2–1 mol). The solvent was slowly given off on standing at room temperature.

Diiodotris(trimethylphosphine)nickel(II). Trimethylphosphine (2.28 g, 3×10^{-2} mol) and nickel iodide (3.12 g, 10^{-2} mol) were refluxed with abs. ethanol (100 ml) until nearly all the nickel iodide had dissolved. The dark green solution, on cooling, deposited dark crystals which were filtered off, washed with abs. ethanol and dried *in vacuo*. Yield 4.00 g (75 %) of violet-black crystals. The pure complex, after recrystallization from abs. ethanol, melted at 160–170°C (decomp.). (Found: C 19.98; H 5.24; I 46.77. Calc. for $\text{C}_9\text{H}_{27}\text{I}_2\text{NiP}_3$: C 19.99; H 5.03; I 46.94). The complex is less soluble than the bromo complex in polar solvents and more soluble in benzene. Solutions are dark green, and when powdered the compound is also green in the solid state.

Chlorotris(trimethylphosphine)nickel(II) perchlorate. A solution of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ (0.47 g, 2×10^{-3} mol) and trimethylphosphine (0.46 g, 6×10^{-3} mol) in abs. ethanol (5 ml)

was mixed with a solution of LiClO_4 (1.0 g) in abs. ethanol (5 ml). Red crystals were slowly deposited from the dark red solution. After 2 h at room temperature, the crystals were isolated by centrifugation, washed with ethanol and dried *in vacuo*. Yield 0.70 g (83 %) of red crystals, m.p. 172–176°C (decomp.). (Found: C 25.53; H 6.27; Cl 16.75. Calc. for $\text{C}_9\text{H}_{27}\text{Cl}_2\text{NiO}_4\text{P}_3$: C 25.62; H 6.45; Cl 16.81). IR-spectrum (KBr, ClO_4^- absorptions only): 1070–1105 cm^{-1} (vs, br), 622 cm^{-1} (s).

Bromotris(trimethylphosphine)nickel(II) perchlorate. LiClO_4 (0.30 g) in abs. ethanol (2 ml) was added to $[\text{NiBr}_2(\text{Me}_3\text{P})_3]$ (0.22 g, 5×10^{-4} mol) in abs. ethanol (2 ml) to give a clear blue-lilac solution. Crystallization was initiated after some minutes by scratching. The dark red-lilac crystals were isolated by centrifugation, washed with ethanol and dried *in vacuo*. Yield 0.12 g (50 %), m.p. 169–170°C (decomp.). (Found: C 23.32; H 5.76; Br 17.38; Cl 7.33. Calc. for $\text{C}_9\text{H}_{27}\text{BrClNiO}_4\text{P}_3$: C 23.18; H 5.84; Br 17.14; Cl 7.60). IR-spectrum (KBr, ClO_4^- absorptions only): 1070–1105 cm^{-1} (vs, br), 623 cm^{-1} (s).

Tetakis(trimethylphosphine)nickel(II) perchlorate. Trimethylphosphine (0.31 g, 4×10^{-3} mol) was added to a solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (0.36 g, 10^{-3} mol) in abs. ethanol (5 ml). The pale red complex, which precipitated at once, was filtered off, washed several times with ethanol and dried *in vacuo*. Yield 0.52 g (92 %). The complex explodes violently on heating to ca. 190°C. (Found: C 25.68; H 6.47; Cl 12.91. Calc. for $\text{C}_{12}\text{H}_{36}\text{Cl}_2\text{NiO}_8\text{P}_4$: C 25.65; H 6.47; Cl 12.62). IR-spectrum (KBr, ClO_4^- absorptions only): 1060–1120 cm^{-1} (vs, br), 623 cm^{-1} (s). Recrystallization from water gave small red crystals of the pure complex, but only in poor yield. A yellow compound, which was formed by decomposition of the complex during recrystallization was removed by extraction with ethanol. The IR-spectrum of this yellow compound (KBr) showed the presence of water, Me_3PO , and ClO_4^- , but the analytical composition varied from one preparation to another.

Acknowledgement. The author is indebted to Professor K. A. Jensen for his encouragement to undertake this work and for helpful discussions.

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Received January 20, 1969.