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An Electron Diffraction Investigation of Nickel Tetrakis-trifluorophosphine, $Ni(PF_3)_4$, in the Vapour Phase

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The molecular structure of nickel tetrakis-trifluorophosphine in the vapour phase has been investigated by electron diffraction. The four PF_3 groups are found to be arranged tetrahedrally around the Ni atom and undergo essentially free rotation about the Ni–P bonds. The molecular parameters are: Ni–P 2.099 (0.003) Å, P–F 1.561 (0.003) Å, ∠Ni–P–F 118.4 (0.3)°.

The molecular structure of nickel tetrakis-trifluorophosphine has special interest for various reasons, 1) the geometrical arrangement around the Ni atom, 2) the possibility of free or nearly free rotation of the PF_3 groups, 3) the length of the Ni–P bond in a compound containing zero-valent nickel. In such compounds the Ni–P bond length is found to be dependent on the inductive effect of the substituents attached to the phosphorus atom.[1]

The sample of $Ni(PF_3)_4$ used in experiments was kindly supplied by Dr. R. Schmutzler.[2]

EXPERIMENTAL

The sample of $Ni(PF_3)_4$ was maintained at a temperature of −27°C and diffraction patterns recorded at nozzle-to-plate distances of 193.59 mm and 480.59 mm, respectively. The nozzle was kept at room temperature, and the wavelength of the electron beam was 0.06484 Å. Four apparently faultless plates were selected at each distance and the photometer traces derived from these were processed in the usual way.[3] The two average modified molecular intensity curves calculated for the two s-ranges considered, were combined to give a single intensity curve extending from $s=1.50$ Å^{-1} to $s=44.25$ Å^{-1}. As the structure determination proceeded the background curves subtracted were re-assessed and the combined molecular intensity curves re-calculated.

The modified molecular intensity may be expressed by the equation [4]

$$I(s)=\text{const.} \sum_{i\neq j}\sum g_{ij/kl}(s)\ \exp(-\tfrac{1}{2}u_{ij}^2s^2)\ (\sin r_{ij}s)/r_{ij}$$

where

$$g_{ij/kl}(s)=\frac{|f_i|\,|f_j|}{|f_k|\,|f_l|}\cos(\Delta\eta_{ij})$$

In this case f_k was put equal to the complex scattering factor for nickel and f_l equal to the phosphorus scattering factor to obtain a Gaussian shape for the nickel-phosphorus peak in the radial distribution (RD) curve.

The distances and u-values estimated from the RD curve were refined by a least-squares procedure applied to the observed combined molecular intensity curves, the above theoretical equation being assumed.*

STRUCTURE ANALYSIS

The experimental and the theoretical intensity curves are shown in Fig. 1, and the corresponding radial distribution curves are reproduced in Fig. 2.

Four-coordinated compounds of nickel usually have square-planar or tetrahedral configurations, but for reasons mentioned below the square-planar configuration can be excluded in the case of nickel tetrakis-trifluorophosphine.

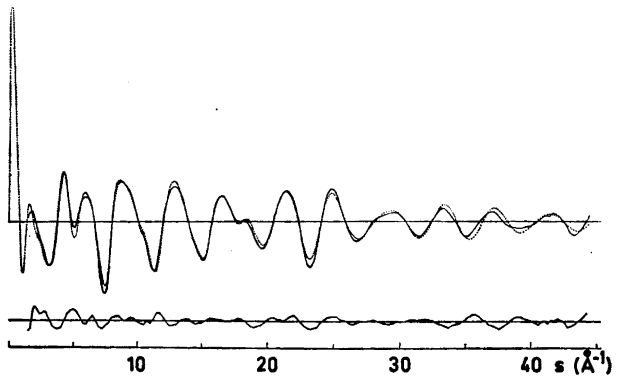

Fig. 1. $Ni(PF_3)_4$. Experimental (———) and theoretical (- - -) molecular intensity curves.

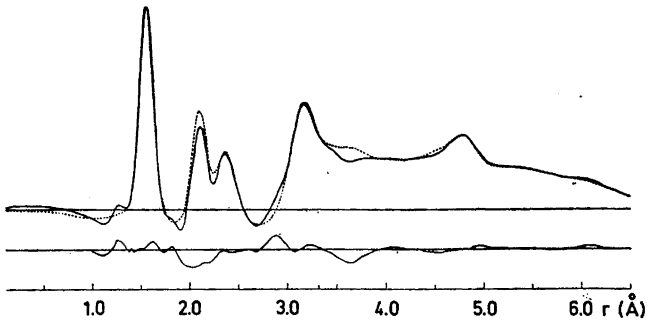

Fig. 2. $Ni(PF_3)_4$. Experimental (———) and theoretical (- - -) radial distribution curves, $k=0.0015$ Å^2.

* The numerical calculations have been carried out on a CDC 3300 computer.[5]

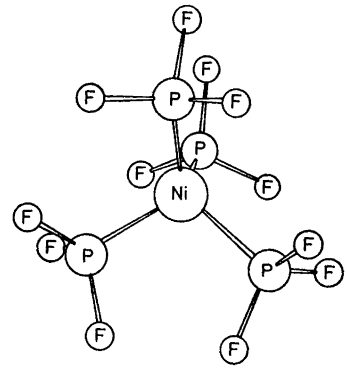

Fig. 3. $Ni(PF_3)_4$.

The experimental RD curve contains five resolved maxima at approximately 1.55 Å, 2.1 Å, 2.36 Å, 3.2 Å, and 4.8 Å.

In a microwave investigation of PF_3[6] the P – F bond length has been shown to be 1.535 Å and the F – P – F angle to be 100°. It seems therefore reasonable to expect that the twelve P – F bond distances in the $Ni(PF_3)_4$ correspond to the peak at 1.55 Å. If the F – P – F angle is put equal to 100° the F···F distances in each PF_3 group will be approximately 2.36 Å. The maximum at 2.1 Å is expected to contain contributions from the Ni – P bond distances. In the tetrahedral model the P···P and the Ni···F interatomic distances are calculated to be about 3.4 Å and 3.15 Å, respectively. This is in good agreement with the peak at about 3.2 Å which has a shoulder at 3.4 Å. The relative heights of the peaks in the experimental RD curves are also consistent with these assumptions.

In Fig. 4 are shown the experimental RD curve, one theoretical RD curve based on a free rotation of the PF_3 groups, and two theoretical curves

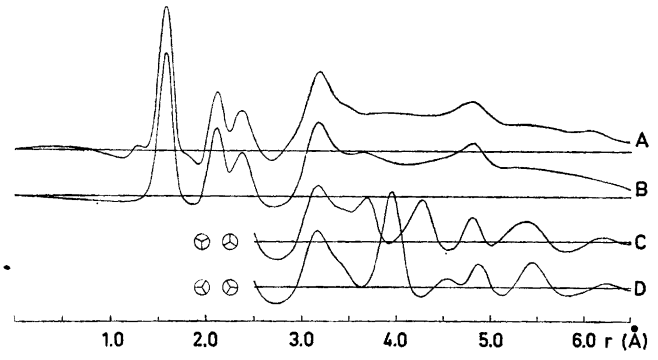

Fig. 4. $Ni(PF_3)_4$. Experimental (A) and theoretical (B,C,D) radial distribution curves. Curve B is calculated for free rotation of the PF_3 groups and C and D for two different rigid conformations, $k = 0.0015$ Å^2. (The position of any two PF_3 groups with respect to each other is given to the left of curve C and D).

based on two arbitrary rigid conformations which differ only in the relative positions of the four PF_3 groups with respect to each other. The inner part of the theoretical curves is identical and the fit to the corresponding part of the experimental curve is satisfactory. From about $r = 3.0$ Å, however, the theoretical curves for the rigid models (curves C and D on Fig. 3) contain maxima which are not present in the experimental curve. It was found that no model which did not include torsional motion is consistent with the experiments. It may therefore be concluded that the PF_3 groups undergo free or slightly restricted rotation, which will cause a smearing out of peaks due to the long F···F and P···F distances.

The computation of the scattering from a freely rotating model was carried out by adding up contributions from configurations obtained by rotating the PF_3 groups in steps of 15°. A better approximation to free rotation could be obtained by decreasing the steps or by increasing the u-values. Because of a lack of computer capacity the great number of distances which would result from the inclusion of smaller steps could not be accommodated, and increased u-values were applied.

That a square-planar model may be excluded can easily be seen from the experimental radial distribution curve for the following two reasons: the square-planar model has more P···F distances that are independent of rotation of the PF_3 groups about the Ni–P bond than the tetrahedral model. These are the P_1F_5, P_1F_6, P_1F_7 and the corresponding distances for P_2, P_3, and P_4 on Fig. 5, which are all about 5.1 Å. There is, however, no peak in this

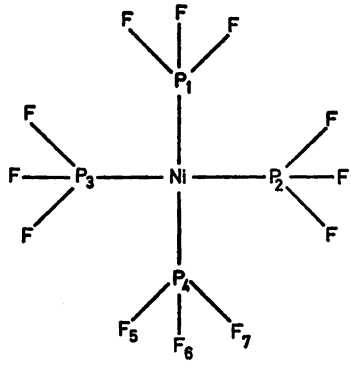

Fig. 5. $Ni(PF_3)_4$. The square-planar model.

region of the experimental radial distribution curve. The peak at 4.8 Å in the experimental radial distribution curve does not correspond to any distance in the square-planar model. The tetrahedral model has six equal P···P distances, while the planar model has four short P···P distances (*i.e.* P_1P_2) and two which are longer (*i.e.* P_1P_4). This means that the tetrahedral model has a greater number of equal P···F distances between different PF_3 groups with contributions to the peak at 4.8 Å than the planar model.

In order to obtain an indication of a possible barrier to rotation of the PF_3 groups a theoretical calculation of the energy of different conformations of

the molecule has been carried out.[7] The distances between the fluorine atoms in different PF_3 groups are always greater than the sum of their van der Waals radii for any twist-angle of one PF_3 group with respect to the neighbouring PF_3 groups. The London energies for the different conformations may be calculated according to:

$$E_v/\varepsilon = -2.25\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736)$$

Here ε is a function of the energy coordinates. The distance between any two rotational dependent atoms is expressed by $\alpha = r/(r_1^* + r_2^*)$ where r is the interatomic distance and r_1^* and r_2^* are the van der Waals radii for these atoms.

The greatest energy difference between any two conformations is found to be 0.4 kcal/mole. Therefore a more or less free rotation should be expected, and this is in agreement with the experimental evidence.

RESULTS AND DISCUSSION

The following molecular parameters have been determined:

Ni–P	2.099 (0.003) Å	u_{NiP}	0.049 (0.005) Å
P–F	1.561 (0.003) Å	u_{PF}	0.034 (0.004) Å
∠P–Ni–P	109.47° (not refined)		
∠Ni–P–F	118.4 (0.3)°		

A fairly satisfactory agreement is obtained between experimental and theoretical curves (Figs. 1 and 2). There are, however, some discrepancies. Because the calculated step-by-step rotation does not correspond to the real rotation of the PF_3 groups, a perfect fit cannot be expected, particularly in the region of the RD curve corresponding to the long F···F distances. For

Table 1. Structure parameters for $Ni(PF_3)_4$. The standard deviations given in parentheses have been corrected [8] to take into account data-correlation and have also been increased to include the uncertainty arising from error in the electron wavelength.[9]

Distances	r (Å)	u (Å)
NiP	2.099 (0.003)	0.049 (0.005)
P–F	1.561 (0.003)	0.034 (0.004)
Ni···F	3.155 (0.005)	0.093 (0.010)
P···P	3.427 (0.007)	0.101 (0.016)
F···F (fluorine atoms in the same PF_3 group)	2.379 (0.005)	0.072 (0.010)
P···F (rotation dependent)	3.592–4.875	0.086
F···F (rotation dependent)	3.064–6.211	0.65
Angles	**degrees**	
∠P–Ni–P	109.47 (not refined)	
∠Ni–P–F	118.4 (0.3)	
∠F–P–F	99.3	

these the u-values have been assumed equal, since individual u-values could not be obtained. As may be seen from Table 1 these u-values are fairly high (0.65 Å) and compensate for the step-by-step rotation of the PF_3 groups, simulating a smooth rotation.

The most obvious disagreement between the experimental and the theoretical radial distribution curves is in the region about 2.1 Å, which contains the peak corresponding to the Ni–P bond distances. In Fig. 2 it is shown that the maximum of this peak corresponds to the same interatomic length in the experimental and the theoretical curves, whereas the area under the curves is greater in the case of the theoretical one. It is reasonable to believe that this disagreement could be due to the applied scattering factor [10] for nickel since a good atomic potential for nickel has not yet become available for calculating this quantity. – As previously mentioned the $Ni(PF_3)_4$ is a zero-valent nickel compound. Nevertheless, there may be a positive or a negative charge on the nickel atom in this molecule. The difference, however, between the scattering factors for Ni and Ni^+ is so small that the effect on the radial distribution curve is negligible.[11,12]

The disagreement between the experimental and the theoretical RD curves at about 3.6 Å may also be explained in terms of an inaccurate nickel scattering factor. Another reason for the discrepancy in this region may be the difference between the calculated free rotation and a rotation which is affected by small energy differences owing to interactions between the fluorine atoms. Such an energy difference may lead to a changing probability for the different relative fluorine-atom positions. Because of the complexity of the rotation in this molecule it has, however, not yet been possible to investigate this problem.

Note added in proof. Recently Marriott *et al.*[13] have published the results of an independent electron diffraction investigation of nickel tetrakis-trifluorophosphine. Their values for the bond distances and bond angles are in good agreement with ours. However, there are certain puzzling differences between the two sets of parameter values involving the rotation-sensitive distances. We are currently investigating this disagreement.

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