THE PREPARATION AND INFRA-RED SPECTRUM OF TETRAKISTRIIODOPHOSPHINE-NICKEL(0), $Ni(PI_3)_4$

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ABSTRACT

The preparation of tetrakistriiodophosphine-nickel(0) as an unstable violet-black solid is reported for the first time. The infrared spectrum is assigned on the basis of the T_d molecular point group.

INTRODUCTION

The nickel(0) phosphine compounds, Ni(PX₃)₄, where X = F and Cl, have been known for some time [1, 2] and have been characterised spectroscopically [3-6]; the vibrational assignments were consistent with the molecular point group T_d . The compound Ni(PBr₃)₄ has also been reported [2] as an unstable solid but this has only recently been obtained pure and analysed using vibrational spectroscopy [7]. In this work, the compound Ni(PI₃)₄ is prepared for the first time and its stability compared with other members of the Ni(PX₃)₄ series.

EXPERIMENTAL

Preparation of $Ni(PI_3)_4$

A method of preparation analogous to that which was used in the successful preparation of a pure sample of Ni(PBr₃)₄ [7] was adopted, namely the displacement of phosphorus(III) chloride from the Ni(PCl₃)₄ complex by excess phosphorus(III) iodide; the trapping out of phosphorus(III) chloride assists the completion of the reaction

 $Ni(PCl_3)_4 + 4PI_3 \Rightarrow Ni(PI_3)_4 + 4PCl_3$

Phosphorus(III) iodide is a deep red solid (m.p. 66°C) prepared by refluxing white phosphorus and iodine in carbon disulphide [8]. The solid fumes in moist air and reacts with oxygen, hence the solvents used in the preparation must be vacuum-distilled and sodium dried before use.

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Since both tetrakistrichlorophosphine-nickel(0) and phosporus(III) iodide are solids, the solvent chosen for the reaction was n-hexane, in which both are fairly soluble without extensive decomposition. $2 \text{ g of } Ni(PCl_3)_4$ was dissolved in dried, vacuum-distilled n-hexane (b.p. 67°C) and 8 g PI₃, which represents a 60% excess over the stoichiometry required by the equation, was similarly treated but with gentle warming to ~ 303 K to effect solution. The two solutions were mixed at room temperature in a flask under an atmosphere of nitrogen; the phosphorus(III) chloride evolved was condensed in two traps cooled to 195 K by solid carbon dioxide. The bright orange solution of phosphorus(III) iodide became black in colour almost immediately on mixing with the solution of $Ni(PCl_3)_4$. Warming the reaction mixture to assist complete conversion to the iodo complex is not advisable because immediate decomposition to nickel occurs on the walls of the flask. A similar situation had already been reported for the preparation of the tetrakistribromophosphine-nickel(0) species [7]. To complete the reaction as far as possible the reaction flask was attached to a rotary pump, via two traps cooled to 77 K by liquid nitrogen, and pumped for about 1 h.

On cooling the reaction mixture to 195 K in an acetone—carbon dioxide bath, deep violet-black crystals were obtained. These crystals fume in moist air and darken on exposure to light with the formation of nickel deposits at the surface.

It was necessary to carry out between three and five further recrystallisations from n-hexane at 195 K to obtain samples which gave the following analysis results: found; %Ni = 3.60, %I = 89.15; required for Ni(PI₃)₄, %Ni = 3.44, %I = 89.29.

It seems reasonable to assume, therefore, that the species $Ni(PI_3)_4$ has been prepared.

Vibrational spectra

Raman spectra were excited using the 632.8 nm line of a helium—neon laser (power 30 mW at the sample) and a Spex Instruments 1401 double monochromator with photon-counting detection. The photomultiplier detector was a red-sensitive ITT FW/130. Data acquisition and spectrometer control was carried out using a Nicolet Instruments NIC 1180 computer. Calibration of the Raman spectra was effected using neon emission lines and vibrational wavenumbers are accurate to ± 1 cm⁻¹.

Infrared spectra of the Ni(PI₃)₄ samples were recorded with Nujol mulls using a Beckmann IR-11 spectrometer (800–33 cm⁻¹ range) and polythene disc plates. Calibration was effected using indene spectra and the vibrational wavenumbers are accurate to ± 1 cm⁻¹.

The violet-black solid which was analysed as $Ni(PI_3)_4$ dissolves in hydrocarbons to give orange solutions which immediately decompose at room temperature. The solid was too darkly coloured and the solutions found to be too unstable for Raman excitation; even with cooled n-hexane solutions at 225 K under laser irradiation the decomposition was too rapid for a Raman spectrum to be obtained. The thermal instability of this compound fits into the observed pattern with other members of the Ni(PX₃)₄ series (X = F, Cl and Br) where the instability increases as X becomes larger, especially in hydrocarbon solvents. Hence, vibrational spectroscopic studies of Ni(PI₃)₄ were limited to the infrared.

The nickel complex proved to be very unstable in the infrared beam also at ambient temperature, but the infrared spectra could be obtained successfully at 225 K using a jacketted cell with polythene windows and nitrogen coolant. Even with cooling precautions being taken, the samples were found to decompose in the infrared beam after several minutes, when vibrational bands of phosphorus(III) iodide could be used to readily identify this material as the decomposition product. The infrared spectrum of Ni(PI₃)₄ shown in Fig. 1 is a composite of several spectra recorded successively with freshly mulled samples.

The wavenumbers in the infrared spectrum of solid phosphorus(III) iodide and in the Raman spectrum of phosphorus(III) iodide in n-hexane solution are shown in Table 1. The wavenumbers in the infrared spectrum of $Ni(PI_3)_4$ are given in Table 2.



Fig. 1. Infrared spectrum, 50-400 cm⁻¹, of tetrakistriiodophosphine-nickel(0); nujol mull.

TABLE 1

Wavenumbers and assignments in the infrared and Raman spectra of phosphorus(III) iodide

Infrared (solid)	Raman (solution in n-hexane)	Assignment and approx. description of mode
75 mw	79 m, depol.	ν_4 (e) PI ₃ deformation
108 mw	111 m, pol.	ν_2 (a ₁) PI ₃ deformation
300 m	302 s, pol.	$\nu_1(a_1)$ PI stretch
325 s	325 m, depol.	$\nu_3(e)$ PI stretch

TABLE 2

Infrared (solid)	Assignment and approx. description of mode	
329 m	ν_{13} P–I asymmetric stretch	
318 m	ν_{14} P–I symmetric stretch	
184 m	ν_{15} NiP asymmetric stretch	
164 mw, sh.	ν_{16} PI ₃ symmetric deformation	
158 m	ν_{17} PI ₃ asymmetric deformation	
70 w, br.	ν_{1} PI ₃ rock	
	ν_{19} NiP ₄ deformation	

Wavenumbers and assignments in the infrared spectrum of tetrakistriiodophosphinenickel(0)

RESULTS AND DISCUSSION

On the basis of T_d molecular point group symmetry the vibrational modes of Ni(PI₃)₄ have the following distribution:

 $\Gamma_{\rm vib} = 3A_1 + A_2 + 4E + 4F_1 + 7F_2$

Of these, the species A_1 , E and F_2 will be active in the Raman and only the F_2 species will have infrared activity. Assignment of the vibrational infrared spectrum in Table 2 can be made by comparison with Ni(PF₃)₄ [4], Ni(PCl₃)₄ [5], Ni(PBr₃)₄ [6] and with the vibrational spectrum of PI₃ in Table 1. The Raman spectrum of PI₃ reported here is in essential agreement with that reported in an earlier study [8].

The bands of medium intensity at 329 and 318 cm⁻¹ are assigned to the P–I asymmetric and symmetric stretching vibrations, respectively, ν_{13} and ν_{14} of the Ni(PI₃)₄ molecule, F_2 symmetry class. The band at 184 cm⁻¹ is assignable to v_{15} , the Ni–P asymmetric stretching vibration, which occurs at 189 cm⁻¹ in Ni(PBr₃)₄, 203 cm⁻¹ in Ni(PCl₃)₄ and at 219 cm⁻¹ in the infrared spectrum of Ni(PF₃)₄. The bands at 164 and 158 cm⁻¹ are assigned to ν_{16} and v_{17} , the PI₃ symmetric and asymmetric deformations, respectively. It should be noted, however, that a spectroscopic inversion of the assignment of these deformations could be possible by analogy with the bromo compounds, $Ni(PBr_3)_4$ and PBr_3 . In the case of $Ni(PBr_3)_4$ [7], the symmetric and asymmetric PBr_3 deformations are inverted with respect to PBr_3 and the assignment of these deformations in the metal-phosphine complex is the same as that in POBr₃. A similar situation could apply to Ni(PI₃)₄. The assignment of ν_{18} , PI₃ rocking to the broad infrared band at 70 cm⁻¹ follows by analogy with other Ni(PX₃)₄ species. The remaining vibrational mode, ν_{19} , would be expected around 40 cm^{-1} or lower and is not observed here.

It may be concluded that the infrared spectrum of the molecule $Ni(PI_3)_4$ is consistent with the T_d molecular point group as are the other members of the Ni(PX₃)₄ series, where X = F, Cl and Br. It must be pointed out that the



Fig. 2. Correlation diagram of $Ni(PX_3)_4$ molecules, X = F, Cl, Br and I.

quality of the observed infrared spectrum in Fig. 1 is not sufficient to exclude the possibility of a molecular symmetry for Ni(PI₃)₄ which is lower than T_d , for example C_{3v} . However, the overall appearance of the infrared spectrum and the spectral line-widths are very similar to the infrared spectrum observed for Ni(PBr₃)₄ [7], for which there is supporting Raman spectroscopic evidence for the T_d molecular assignment. In particular, the progression through the series of the ν (Ni-P) asymmetric stretch from Ni(PF₃)₄ and referred to above is noteworthy.

In Fig. 2, the correlation from Ni(PF₃)₄ through to Ni(PI₃)₄ is presented and gives an estimated vibrational band position for ν (Ni–P) stretching in the latter species. Simple calculations based on Ni(PBr₃)₄ and mass changes in substitution of the I for Br, without allowance being made for force constant or interaction force constant changes, reveal that the ν (Ni–P) symmetric stretching wavenumber (Raman active) would be expected at ~55 cm⁻¹ cf. 219 cm⁻¹ for the Ni(PF₃)₄ species.

In conclusion, it is believed that the infrared vibrational spectroscopic data are consistent with the assignment of the Ni(PI₃)₄ species to a molecular point group of T_d in common with the earlier members of the series, viz. Ni(PF₃)₄, Ni(PCl₃)₄ and Ni(PBr₃)₄.

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