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SPECTROSCOPIC AND THERMODYNAMIC INVESTIGATIONS OF GROUP V HALIDES

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MAY 1977

FINAL REPORT FOR PERIOD JANUARY 1972 - DECEMBER 1975

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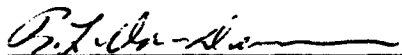
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MR. FREEMAN F. BENTLEY
Project Monitor

FOR THE COMMANDER



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Block 20 Continued:

P_2Cl_9Br , $PCl_3Br^+BC_4^-$, $PBr_4^+IBr_2^-$, PCl_4^- , ICl_4^- , $PCl_4^+ICl_2^-$ and NI_3NH_3 .

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FOREWORD

This report was prepared by Royal Holloway College, Egham, Surrey TW20 OEX England under Grant AFOSR-72-2196, Project No. 7367, "Experimental Techniques for Materials Research", Task No. 736702, "Physical Chemical Methods for Materials Analysis", with Mr. Freeman F. Bentley (AFML/MBP) as project engineer.

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The research described in this report was performed at the Royal Holloway College, England by Dr. Arthur Finch of the Department of Chemistry. The manuscript was released by the author in March 1976 for publication as a technical report.

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SECTION I

Introduction

In the four years covered by this Final Report various aspects of the chemistry of some Group V compounds have been investigated. These aspects may be summarised as follows:

1. An investigation of "normal" and "metastable" PCl_5 by differential scanning calorimetry.
2. Preparation and spectroscopic investigation of some fluorine-containing mixed halogen phosphorus (V) species.
3. Preparation and spectroscopic investigation of some mixed cyanide-halide phosphorus (V) compounds.
4. Calorimetric investigation of some mixed chloro-bromo phosphorus (V) compounds.
5. Calorimetric investigation of $\text{NI}_3 \cdot \text{NH}_3(\text{c})$.

Some aspects of these investigations are incomplete as yet and other sections of it are being prepared for publication in the scientific literature.

SECTION II

1. Investigation of "Normal" and "Metastable" PCl_5 by Differential Scanning Calorimetry

Following observations by Shore and Knachel¹ on the Raman spectra of the two forms of PCl_5 and subsequent investigation in these Laboratories², further study has been made using differential scanning calorimetry. In summary, the Raman spectra showed significant differences between the "normal" form (in which the frequencies for the PCl_4^+ and PCl_6^- species are similar to those in other species containing these ions) and the "metastable"

form in which the band positions of the PCl_4^+ ion are shifted and relative band intensities of the ions are reversed. One possibility is that the metastable form may contain some Cl^- ions in the crystal lattice, replacing some of the PCl_6^- ions such that the overall stoichiometry remains as PCl_5 . Alternatively, the metastable form may simply involve a rearrangement of the ions in the crystal lattice, possibly accounting for the observed spectral changes.

The differential scanning calorimetry of the two forms was carried out in an attempt to establish any difference in the thermograms of the two and to attempt to measure the heat of transition from the metastable to the normal form. Results are detailed below:

Normal PCl_5

In the range $40^\circ - 165^\circ\text{C}$ only one transition was observed for normal PCl_5 . This occurred at 110°C and was endothermic and reversible with a value for the heat of transition of $+1.97 \pm 0.08 \text{ kJmol}^{-1}$. The corresponding entropy change was $+5.14 \text{ J mol}^{-1}\text{K}^{-1}$. The nature of this crystalline transition is not known and is apparently unreported.

Metastable PCl_5

In the range $40^\circ - 165^\circ\text{C}$ two transitions were observed for metastable PCl_5 : a reversible endotherm at $111^\circ \pm 2^\circ$ which is clearly identified with the endotherm at this temperature in normal PCl_5 and an irreversible exotherm at $130^\circ \pm 4^\circ\text{C}$. On re-running the sample through a similar temperature range, no exotherm was observable and the thermogram resembled closely that derived from "normal" PCl_5 . It is therefore reasonable to identify the exotherm from the metastable PCl_5 with a PCl_5 (metastable) $\rightarrow$ PCl_5 (normal) transition. Experimental difficulties, which were severe, preclude precise measurements, but transition enthalpies of the order of 80 kJmol^{-1} are indicated.

The absence of exotherms both in normal and the transformed PCl_5 give good evidence for the integrity of the system, since any reaction, for

example with the aluminium pan of the calorimeter or through atmospheric moisture, would result in observed exothermic peaks.

2. Fluorine-containing Mixed Halide Complexes of Phosphorus (V)

Following earlier investigations in these Laboratories^{2,3,4,5} on the preparation and vibrational spectra of some mixed chloro-bromo phosphorus (V) species an extension to some further mixed halide species containing fluorine was initiated.

This work was concentrated mainly on the reaction of PCl_2F with Cl_2 or Br_2 . Although the previous⁵ characterisation (by Raman spectroscopy) of the ions PCl_3Br^+ , $\text{PCl}_2\text{Br}_2^+$ and PClBr_3^+ has allowed the recognition of these ions in the products of reaction of Cl_2 or Br_2 with PCl_2F , it has unfortunately not been possible to formulate the nature of these reaction products precisely.

Reaction of PCl_2F with Cl_2

Numerous reactions of this type have been carried out in the course of this work. In a typical reaction, chlorine was condensed on to PCl_2F at -78°C . Initially, a small amount of a white solid, A, was precipitated. This was isolated by removal of the remaining liquid under vacuum into a trap at -196° . On standing at room temperature the liquid gradually changed into a white solid, B. Infrared and Raman band positions are listed in Table 1 and the Raman spectra shown in Figs. 1 and 2.

The Raman spectrum of the white solid, A, clearly shows (Fig. 1) the bands due to the PCl_4^+ ion ($654, 458, 250$ and 170 cm^{-1}) at positions associated with the absence of single halide ions in the lattice. Apart from these bands a number of other bands are observed (see Table 1). The infrared spectrum (Table 1) is also too complex for a simple formulation like PCl_4^+F^- and in addition shows the presence of absorptions due to P-F bonds. It is possible that a formulation such as $\text{PCl}_4^+\text{PCl}_4\text{F}_2^-$ occurs

with a centrosymmetric (D_{4h}) $PCl_4F_2^-$ ion. The lack of coincidences in the infrared and Raman spectra are consistent with such a structure. The white solid, B, gives a very simple Raman spectrum (Fig. 2) which shows only lines due to the PCl_4^+ ion, at frequencies associated with the presence of a single halide ion in the lattice. Initially it was thought that this was consistent with a formulation of $PCl_4^+F^-$, but an infrared spectrum clearly indicates the presence of P-F bonds in the compound. Moreover, simple dissolution of the complex in water followed by analysis for F^- by a fluoride ion electrode, does not reveal the total fluorine content expected on the basis of the simple $PCl_4^+F^-$ formulation. On standing at room temperature for several days, or on heating at 120° overnight, the Raman spectrum of compound A changes to that corresponding to compound B. Further investigation into the products of these reactions will be made.

Reaction of PCl_2F with Br_2

A number of reactions between these species have been carried out (for a typical reaction see the Experimental Section) yielding products with varying analyses.

The Raman spectrum of a typical reaction product is shown in Fig. 3. From this (and Table 2) it can be seen that the bands characteristic⁵ of PCl_3Br^+ , $PCl_2Br_2^+$ and $PClBr_3^+$ were all present, the frequencies being those previously associated with the presence of single halide ions in the lattice. The relative peak heights of the Raman bands vary with the preparation, indicating that the mixture formed varies, this being consistent with the analytical results. All attempts to prepare a compound containing only one of the chlorobromophosphonium ions were unsuccessful. All bands can be accounted for on the basis of the various mixed chlorobromophosphonium ions and there are no signs of emissions due to any anionic species. This must mean either (a) that the anionic species is a relatively very poor Raman scatterer or (b) that the anionic species is

F^- , in which case the complexes could be generally formulated as $PCl_{4-n}Br_n^+F^-$ ($1 \leq n \leq 3$). In either case, the characteristic frequencies suggest that halide ions may be present in the crystal lattice.

(iii) Reaction between PCl_5 and AsF_3 in $AsCl_3$

The reaction between PCl_5 and AsF_3 in $AsCl_3$ at $75^\circ C$ has been reported to yield ionic PCl_4F .⁶ Since the nature of the initial (compound A) and final (compound B) species (see Section 2 (i) above) has yet to be firmly established, this reaction was further investigated in an attempt to determine whether the product could be identified with either A or B. The Raman and infrared spectra clearly identify this material with compound B.

3. Cyanide-containing Mixed Halide Complexes of Phosphorus (V)

Various reactions have been investigated in an attempt to prepare some complexes of this type. The only previously-reported species are $R_4N^+ PCl_4(CN)_2^-$ (where R = n-butyl and n-propyl)⁷ together with some work on the reaction of PCl_5 with some cyanides⁸.

In the course of the present work two severe experimental difficulties have arisen which have effectively precluded any positive conclusions: (i) with the exception of the $R_4N^+ PCl_4(CN)_2^-$ compounds the various reactions only produced very small amounts of extremely unstable solids which were very difficult to handle and (ii) it has proved impossible to obtain Raman spectra, even for the $R_4N^+ PCl_4(CN)_2^-$ compounds.

The following approaches were made:

a. Reaction of $P(CN)_3$ with Cl_2 or Br_2

In several experiments Cl_2 was condensed onto $P(CN)_3$, allowed to liquefy and held at $-78^\circ C$. On removal of the liquid, unchanged $P(CN)_3$ remained. Similar mixtures of Br_2 with $P(CN)_3$ resulted in the recovery of unchanged $P(CN)_3$ except where a large excess of Br_2 was used in which case the product was PBr_5 .

b. Reaction of PCl_5 with AgCN

It has been previously claimed⁸ that reaction of AgCN with PCl_5 in 1:1 molar proportions in acetonitrile or dichloromethane yields a product of stoichiometry PCl_4CN . These reactions were reinvestigated as it seemed likely that the complex PCl_4CN might have a structural formulation $\text{PCl}_4^+\text{PCl}_4\text{CN}_2^-$. Some very unstable white solids in low yield were produced by these reactions (see Experimental Section). A comparison of the infrared spectrum with that of $\text{R}_4\text{N}^+\text{PCl}_4(\text{CN})_2^-$ suggested that a common ion might exist in the two species.

c. Preparation and vibrational spectra of $\text{R}_4\text{N}^+\text{PCl}_4(\text{CN})_2^-$ complexes
($\text{R} = n$ propyl and n -butyl)

These were prepared, following Roesky⁷, by addition of KCN to PCl_5 in acetonitrile solution followed by addition of aqueous tetraalkylammonium chloride solution. All attempts to obtain a Raman spectrum of the white solids were unsuccessful but infrared bands for the two salts are listed in Table 3. In the absence of the Raman spectrum it has not been possible to infer the geometry of the $\text{PCl}_4(\text{CN})_2^-$ ion but the infrared spectra are sufficient to indicate an identity of this species with that produced from reaction of PCl_5 with AgCN (see 3 b. above).

4. Solution-Reaction Calorimetry of Various Phosphorus (V) Halide Species

Thermodynamic properties of several halogen and mixed-halogen phosphorus (V) species have been investigated in the course of this project. These are summarised below:

- (a) Trichlorobromophosphonium tetrachloroborate ($\text{PCl}_3\text{Br}^+\text{BCl}_4^-$).
- (b) $\text{P}_2\text{Cl}_9\text{Br}$.
- (c) Tetrabromophosphonium dibromiodide ($\text{PBr}_4^+\text{IBr}_2^-$).
- (d) Tetrachlorophosphonium dichloriodide ($\text{PCl}_4^+\text{ICl}_2^-$).
- (e) Tetrachlorophosphonium tetrachloriodide. ($\text{PCl}_4^+\text{ICl}_4^-$).

For each of these a suitable calorimetric reaction has been established.

The measured heats of reaction for these processes are summarised in Tables 4 - 8. Standard enthalpies of formation, ΔH_f° were calculated using the following equations and appropriate ancillary data:

$$(a) \quad \Delta H_f^\circ(\text{PCl}_3\text{BrBCl}_4, c) = \Delta H_f^\circ(\text{H}_3\text{PO}_4, 10,000 \text{ H}_2\text{O}) + \Delta H_f^\circ(\text{B}(\text{OH})_3, 20,000 \text{ H}_2\text{O}) \\ + 7\Delta H_f^\circ(\text{HCl}, 3,000 \text{ H}_2\text{O}) + \Delta H_f^\circ(\text{HBr}, 20,000 \text{ H}_2\text{O}) \\ - 7\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_R.$$

$$(b) \quad \Delta H_f^\circ(\text{P}_2\text{Cl}_9\text{Br}, c) = 2\Delta H_f^\circ(\text{H}_3\text{PO}_4, 10,000 \text{ H}_2\text{O}) + 9\Delta H_f^\circ(\text{HCl}, 10,000 \text{ H}_2\text{O}) \\ + \Delta H_f^\circ(\text{HBr}, 100,000 \text{ H}_2\text{O}) - 8\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_R.$$

$$(c) \quad 3\Delta H_f^\circ(\text{PBr}_4\text{IBr}_2, c) = 18\Delta H_f^\circ(\text{AgBr}, c) + 2\Delta H_f^\circ(\text{AgI}, c) + \Delta H_f^\circ(\text{AgIO}_3, c) \\ + 21\Delta H_f^\circ(\text{HNO}_3, 5,500 \text{ H}_2\text{O}) + 3\Delta H_f^\circ(\text{H}_3\text{PO}_4, 10,000 \text{ H}_2\text{O}) \\ - 21\Delta H_f^\circ(\text{AgNO}_3, 5,000 \text{ H}_2\text{O}) - 15\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_R.$$

$$(d) \quad 3\Delta H_f^\circ(\text{PCl}_4\text{ICl}_2, c) = 18\Delta H_f^\circ(\text{AgCl}, c) + 2\Delta H_f^\circ(\text{AgI}, c) + \Delta H_f^\circ(\text{AgIO}_3, c) \\ + 21\Delta H_f^\circ(\text{HNO}_3, 7000 \text{ H}_2\text{O}) + 3\Delta H_f^\circ(\text{H}_3\text{PO}_4, 10,000 \text{ H}_2\text{O}) \\ - 21\Delta H_f^\circ(\text{AgNO}_3, 500 \text{ H}_2\text{O}) - 15\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_R.$$

$$(e) \quad 3\Delta H_f^\circ(\text{PCl}_4\text{ICl}_4, c) = 24\Delta H_f^\circ(\text{AgCl}, c) + \Delta H_f^\circ(\text{AgI}, c) + 2\Delta H_f^\circ(\text{AgIO}_3, c) \\ + 27\Delta H_f^\circ(\text{HNO}_3, 5,000 \text{ H}_2\text{O}) + 3\Delta H_f^\circ(\text{H}_3\text{PO}_4, 10,000 \text{ H}_2\text{O}) \\ - 27\Delta H_f^\circ(\text{AgNO}_3, 5,000 \text{ H}_2\text{O}) - 18\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_R.$$

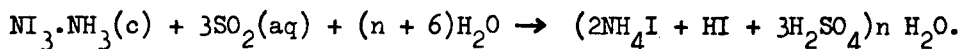
The standard enthalpies of formation are collected in Table 9.

5. Thermochemical Investigation of $\text{NI}_3 \cdot \text{NH}_3$

$\text{NI}_3 \cdot \text{NH}_3$ is usually regarded as a highly unpredictable and unstable species likely to explode on drying or mechanical shock.⁹ It has been the subject of two previous thermochemical investigations, one by solution reaction calorimetry¹⁰ employing reaction with aqueous HI yielding a value for $\Delta H_f^\circ(\text{NI}_3 \cdot \text{NH}_3, c)$ of $+146.4 \text{ kJmol}^{-1}$ and another by bomb calorimetry¹¹

leading to the value of $+49.1 \pm 8 \text{ kJmol}^{-1}$. The current work was initiated in an attempt to resolve this discrepancy and is, as yet, incomplete.

$\text{NI}_3 \cdot \text{NH}_3$ is very difficult to handle and at 25°C in water decomposes substantially in the time necessary for equilibration of the calorimeter. It is also light sensitive. Accordingly, the calorimeter was shielded from light and the reaction carried out at 12.5°C in order to minimise decomposition during equilibration. Decomposition is further suppressed by the presence of aqueous ammonia. It was impossible to weigh out samples of the dry $\text{NI}_3 \cdot \text{NH}_3$ and hence the freshly prepared samples were loaded in the ampoule under a known volume of standard aqueous ammonia (in order to reduce the rate of decomposition) and the amount of $\text{NI}_3 \cdot \text{NH}_3$ estimated by iodide analysis after each calorimetric reaction. The calorimetric reaction employed involved reduction with aqueous SO_2 solution as follows:



Heats of reaction (ΔH_R) referring to this process are summarised in Table 10. A series of "blank" determinations were carried out by breaking ampoules containing the same volume of the aqueous ammonia solution (used to suppress the decomposition of $\text{NI}_3 \cdot \text{NH}_3$) into the aqueous SO_2 solution. From this, the heat associated with reaction of the two solutions could be corrected for. The mean (from 4 values) heat for the $\text{SO}_2 \text{ aq} + \text{NH}_3 \text{ aq}$ reaction is $68.66 \pm 1.05 \text{ kJmol}^{-1}$.

Employing the above equation and heat of formation data for SO_2 , H_2O , NH_4I , HI and H_2SO_4 under the appropriate dilution conditions, a value for $\Delta H_f(\text{NI}_3 \cdot \text{NH}_3, \text{c})$ of $+23.9 \pm 6.2 \text{ kJmol}^{-1}$ was calculated. This positive value is to be expected in view of the explosive nature of the compound but there is a considerable discrepancy with the earlier reported values of $+146.4^{10}$ and $+49.1^{11} \text{ kJmol}^{-1}$. In view of this it is desirable to confirm our result using a different calorimetric reaction. It is proposed to employ reaction of the system with HCl as follows:



if this proves to be suitable. This work is in progress at present.

Preparation and Analysis of Compounds

Preparation of PCl_2F

This was prepared following the method of Holmes et al¹² by the gradual addition of powdered, dried SbF_3 (180 g, 1 mol) to PCl_3 (140 g, 1 mol) at 40° and 240 mm Hg with stirring. SbCl_5 (1 cm³) was added to act as a catalyst. Gaseous products were collected in a trap at -196° . These comprised PCl_3 , PCl_2F , PClF_2 and PF_3 . Pure PCl_2F was obtained by repeated trap to trap fractionation.

Reaction of PCl_2F with Cl_2

In a typical reaction, chlorine was condensed on to PCl_2F at -78°C . Initially a small amount of white solid, A, was precipitated. This was isolated by the removal of the remaining liquid under vacuum into a trap at -196° . On standing at room temperature the liquid gradually changed into a white solid B. Analyses are summarised below:

	Found		calc. for PCl_4F	
	% Cl	% F	% F	% Cl
Initial White Solid, A.	77.9		9.9	74.0
White Solid, B.	72.6	5.7		

Reaction of PCl_2F with Br_2

Various reactions of this type have been carried out, yielding products with varying analyses. In a typical reaction, PCl_2F (13.55 g, 0.112 mol) and bromine (17.70 g, 0.111 mol) were condensed into a flask at -196° and the mixture allowed to warm to room temperature. The result-

ing yellowish-red solid was pumped for 1 hour. (See section 2(ii)).

Reaction between PCl_5 and AsF_3 in AsCl_3

AsF_3 (8.73 g, 0.066 mol) was added dropwise to a solution of PCl_5 (40.0 g, 0.192 mol) in AsCl_3 at 75°C . White fumes appeared with addition of the last few drops of AsF_3 . The resultant mixture was allowed to stand at 0°C for 15 hours and filtered to yield a white solid where Raman and infrared spectra are identical to those for compound B (above).

Preparation of $\text{P}(\text{CN})_3$

AgCN (50 g, 0.37 mol) was finely ground and mixed under nitrogen with PCl_3 (32.0 g, 0.24 mol) in benzene (50 cm^3). The mixture was refluxed at 80° for 24 hours. Benzene and excess PCl_3 were distilled off and the crude grey product dried under vacuum for 2 hours. On sublimation at $110^\circ\text{C}/0.05\text{ mm Hg}$ white crystals of $\text{P}(\text{CN})_3$ were obtained. This material was used without further purification for reaction with (a) Cl_2 and (b) Br_2 .

Reaction of $\text{P}(\text{CN})_3$ with Cl_2

A small amount of $\text{P}(\text{CN})_3$ contained in a tube was attached to a vacuum line and Cl_2 in excess was condensed onto it at -196°C . The Cl_2 was allowed to liquefy and held at -78°C . A white solid remained which was identified (Raman spectrum) as unchanged $\text{P}(\text{CN})_3$.

Reaction of $\text{P}(\text{CN})_3$ with Br_2

Several reactions of this type were carried out with variation of relative proportions of reactants and solvents. In most cases no reaction occurred but with Br_2 in a large excess over $\text{P}(\text{CN})_3$ in CH_3CN , PBr_5 (identified by the Raman spectrum) was produced.

Reaction of AgCN with PCl_5

Various reactions have been carried out in an attempt to repeat the

previous report⁸ of the preparation of PCl_4CN . In a typical reaction, AgCN (2.44 g, 0.018 mol) and PCl_5 (3.31 g, 0.016 mol) were mixed together in CH_3CN (60 cm^3) and the mixture stirred at ambient temperature for 20 hours. The grey precipitate (AgCl) was filtered off the filtrate cooled at -78°C when a white solid settled out. Similar preparations have been attempted in CH_2Cl_2 .

Preparation of $\text{R}_4\text{N}^+\text{PCl}_4\text{CN}_2^-$ (R = n-propyl)

In a typical reaction PCl_5 (17.3 g, 0.084 mol) was dissolved in CH_3CN (35 cm^3) and heated with KCN (27.5 g, 0.42 mol) with vigorous stirring at $45-50^\circ\text{C}$ for 30 min. After filtering, a 1% aqueous solution of tetra-n-propylammonium chloride was added dropwise to the dark brown filtrate. Reaction was violent to give a brownish precipitate which was subsequently dissolved in acetone and reprecipitated by addition of water. After several repetitions of the procedure a white solid was obtained.

Preparation of $\text{PCl}_3\text{Br}_4^+\text{BCl}_4^-$

BCl_3 (3.9 g, 0.034 mol) was dissolved in liquid HCl at -95°C and PCl_3 (4.2 g, 0.030 mol) followed by Br_2 (3.86 g, 0.024 mol) were added to form a white precipitate. Warming to room temperature followed by pumping left a white solid (Found: Cl, 65.2%, Br, 22.3%. Calc. for PBCl_7Br : Cl, 67.1%; Br, 21.6%).

Preparation of $\text{P}_2\text{Cl}_9\text{Br}$

Br_2 (19.1 g, 0.24 mol) was added dropwise to a solution of PCl_3 (31.6 g, 0.23 mol) in AsCl_3 (30 cm^3). The pale yellow crystalline precipitate was filtered, washed with AsCl_3 and benzene and dried in vacuo. (Found: Cl, 69.4; Br, 17.5%. Calc. for $\text{P}_2\text{Cl}_9\text{Br}$: Cl, 69.2; Br, 17.3%).

Preparation of $\text{PBr}_4^+\text{IBr}_2^-$

IBr (18.6 g, 0.090 mol) dissolved in CH_2Cl_2 (200 cm^3) was added

dropwise to a stirred solution of PBr_5 (35.1 g, 0.082 mol) in CH_2Cl_2 (350 cm^3) at 0°C to form a deep red, crystalline (needle shaped) product. This was washed with CH_2Cl_2 , filtered and dried in vacuo. (Found: Br, 75.1%; I, 19.8%. Calc. for PBr_6I : Br, 75.2; I, 19.9%).

Preparation of $\text{PCl}_4^+\text{ICl}_2^-$

ICl (19.3 g, 0.12 mol) was mixed with CH_2Cl_2 (20 cm^3) and added dropwise to a stirred solution of PCl_5 (23.5 g, 0.11 mol) in CH_2Cl_2 (250 cm^3) to yield a yellow precipitate. This was dried in vacuo. (Found: Cl, 57.8; I, 34.2%. Calc. for PCl_6I : Cl, 57.4; I, 34.2%).

Preparation of $\text{PCl}_4^+\text{ICl}_4^-$

ICl_3 and PCl_5 were mixed together in 1:1 molar proportions in CH_2Cl_2 . The resulting precipitate was filtered off and dried in the absence of moisture. (Found: Cl, 64.19; I, 29.10%. Calc. for PCl_8I : Cl, 64.24; I, 28.74%).

Preparation of $\text{NI}_3 \cdot \text{NH}_3$

Various methods of preparation of this compound have been reported in the literature, most of which yield amorphous black solids from the addition of aqueous ammonia to aqueous KI_3 .

One preparation, first reported¹³ in 1900 and subsequently¹⁴ (1968) used to produce crystals for an X-ray diffraction study gives copper-coloured needle-shaped crystals. This method of preparation was finally adopted in the present work after initial difficulties in handling the black amorphous materials in the calorimeter.

In a typical preparation, 0.5 M KOH solution (100 cm^3) was cooled to 0°C and to this was added (i) an acidic solution of 0.1 M ICl (1.5 cm^3) and (ii) concentrated aqueous ammonia (10 cm^3). Fine, coppery-coloured needle-shaped crystals separated on standing for 5 minutes.

TABLE 1

INFRARED AND RAMAN SPECTRA OF PRODUCTS FROM REACTIONS OF

PCl_2F with Cl_2

Initial White Solid (A)		White Solid (B)		Assignment	
Raman	Infrared	Raman	Infrared	Raman	Infrared
	854 w		850 s		
			776 s		
	768 s		765 s		
	753 s		750 s		
			675 w		
655 w	654 s	640 m	644 vs	$[\text{PCl}_4^+]$	$[\text{PCl}_4^+]$
	620 s		620 s		
	595 vs		594 s		
	578 vs		575 s		
			555 w		
			535 m		
			525 m		
			497 m		
			475 s		
454 s	450 vs	442 vs	450 s	$[\text{PCl}_4^+]$	$[\text{PCl}_6^-]$
	425 w				
399 m		399 w	394 w		
	389 w				
360 w				$[\text{PCl}_6^-]$	
	379 w		378 w		
			347 w		
	338 w		335 w		
320 m	317 w		320 w		
	300 w		300 w		
274 w				$[\text{PCl}_6^-]$	
266 m					
251 s	250 w	250 m	254 m	$[\text{PCl}_4^+]$	$[\text{PCl}_4^+]$
		190 w			
177 m				$[\text{PCl}_4^+]$	$[\text{PCl}_4^+]$
169 m					

TABLE 2

SOLID-STATE RAMAN FREQUENCIES (cm^{-1}) FOR THE PRODUCT
FROM REACTION OF PCl_2F WITH Br_2

<u>Frequency</u>	<u>Phosphonium Ion</u>	<u>Assignment</u>
633(w)	PCl_3Br^+	$\nu_4(\text{e})$
619(w)	$\text{PCl}_2\text{Br}_2^+$	$\nu_6(\text{b}_1)$
587(w, br)	$\left\{ \begin{array}{l} \text{PCl}_2\text{Br}_2^+ \text{ and} \\ \text{PClBr}_3^+ \end{array} \right.$	$\nu_8(\text{b}_2)$ $\nu_4(\text{e})$
570(w)	PCl_3Br^+	$\nu_1(\text{a}_1)$
522(w)	$\text{PCl}_2\text{Br}_2^+$	$\nu_1(\text{a}_1)$
503(m)	PClBr_3^+	$\nu_1(\text{a}_1)$
493(m)	?	
375(vs)	PCl_3Br^+	$\nu_2(\text{a}_1)$
329(vs)	$\text{PCl}_2\text{Br}_2^+$	$\nu_2(\text{a}_1)$
282(vs)	PClBr_3^+	$\nu_2(\text{a}_1)$
237(s)	PCl_3Br^+	$\nu_5(\text{e})$
201(vs)	$\left\{ \begin{array}{l} \text{PCl}_3\text{Br}^+ \\ \text{PCl}_2\text{Br}_2^+ \end{array} \right.$	$\nu_3(\text{a}_1)$ $\nu_7(\text{b}_1)$
191(s)	$\text{PCl}_2\text{Br}_2^+$	$\nu_3(\text{a}_1)$
174(s)	$\text{PCl}_2\text{Br}_2^+ \text{ and}$ PClBr_3	$\nu_9(\text{b}_2)$
151(s)	$\left\{ \begin{array}{l} \text{PCl}_3\text{Br}^+, \\ \text{PCl}_2\text{Br}_2^+ \text{ and} \\ \text{PClBr}_3 \end{array} \right.$	$\nu_6(\text{e})$ $\nu_5(\text{a}_2)$
133(w)	$\text{PCl}_2\text{Br}_2^+$	$\nu_4(\text{a}_1)$
123(w)	PClBr_3^+	$\nu_6(\text{e})$

TABLE 3

INFRARED SPECTRA (cm^{-1}) OF THE $\text{PCl}_4(\text{CN})_2^-$ ION

$[(\text{C}_3\text{H}_7)_4\text{N}^+][\text{PCl}_4(\text{CN})_2^-]$	$[(\text{C}_4\text{H}_9)_4\text{N}^+][\text{PCl}_4(\text{CN})_2^-]$
2184 (s)	2184 (s)
663 } (s)	663 } (s)
650 }	652 }
580 (s)	580 (s)
490 (s)	490 (s)
443 } (s)	443 } (s)
428 }	430 }
347 (m)	341 (m)
321 } (m)	
310 }	314 (m)
240 (m)	240 (m)
226 (ms)	226 (m)

s, strong; m, medium.

TABLE 4

PBCl₇Br

m(g)	dilution	ΔH_R (kJ mol ⁻¹)
0.4235	9,704	740.6
0.2879	14,274	745.3
0.2044	20,106	749.4
0.1457	28,206	743.0
0.1174	35,005	750.0
0.0729	56,373	751.1
0.1644	24,998	744.8
0.1423	28,880	745.3

$$\text{Mean } \Delta H_R = -746.0 \pm 2.5 \text{ kJ mol}^{-1}$$

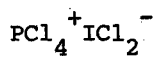
TABLE 5

P₂Cl₉Br

m(g)	dilution	ΔH_R (kJ mol ⁻¹)
0.02139	119,717	1055.7
0.03386	75,629	1043.6
0.03425	74,766	1036.7
0.03565	71,830	1043.0
0.02490	102,841	1035.4
0.02151	119,049	1036.1
0.03910	65,492	1044.9
0.02862	89,474	1048.1
0.02747	93,220	1052.8
0.03252	78,437	1039.2

$$\text{Mean } \Delta H_R = -1043.5 \pm 5.0 \text{ kJ mol}^{-1}$$

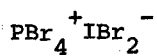
TABLE 6



$m(\text{g})$ $\text{PCl}_4^+ \text{ICl}_2^-(\text{s})$	dilution	$-\Delta H_R (\text{kJ mol}^{-1})$
0.05088	40,465	948.51
0.04703	43,777	941.69
0.04965	41,468	942.61
0.03044	67,637	945.33
0.04391	46,888	948.72
0.03385	60,823	945.17
0.03966	51,913	945.21

$$\text{Mean } \Delta H_R = -945.3 \pm 2.4 \text{ kJ mol}^{-1}.$$

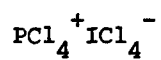
TABLE 7



$m(\text{g})$	dilution	$-\Delta H_R (\text{kJ mol}^{-1})$
0.1992	35,549	1024.7
0.2050	34,544	1024.2
0.1425	49,695	1029.4
0.1269	55,804	1027.3
0.1423	49,764	1026.3
0.1083	65,388	1024.2
0.1520	46,589	1024.1
0.1502	47,147	1022.8
0.1534	46,163	1022.5
0.1801	39,320	1023.4

$$\text{Mean } \Delta H_R = -1024.9 \pm 1.4 \text{ kJ mol}^{-1}.$$

TABLE 8



m(g)	dilution	$-\Delta H_R (\text{kJ mol}^{-1})$
0.01453	42,000	1056.5
0.02186	28,000	1054.6
0.01936	32,000	1054.3
0.02202	28,000	1052.0
0.02028	30,000	1054.8
0.01642	37,000	1056.4
0.02193	28,000	1054.6

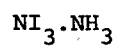
$$\text{Mean } \Delta H_R = -1054.7 \pm 1.3 \text{ kJ mol}^{-1}$$

TABLE 9

STANDARD ENTHALPIES OF FORMATION

Compound	$-\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{PCl}_3 \text{Br}^+ \text{BCl}_4^-$	915.0 ± 2.2
$\text{P}_2\text{Cl}_9\text{Br}$	894.5 ± 6.0
$\text{PBr}_4^+ \text{IBr}_2^-$	966.4 ± 3.8
$\text{PCl}_4^+ \text{ICl}_2^-$	522.3 ± 7.4
$\text{PCl}_4^+ \text{ICl}_4^-$	627.4 ± 6.9

TABLE 10



$m(\text{g})^*$	dilution	$-\Delta H_R (\text{kJ mol}^{-1})$
0.042	100,820	490.9
0.069	66,600	492.9
0.078	58,700	463.9
0.085	54,100	490.5
0.077	59,100	485.1
0.026	177,730	491.0
0.076	60,400	473.2
0.068	66,900	481.2
0.058	79,400	472.9
0.100	45,500	476.2

$$\text{Mean } \Delta H_R = -481.8 \pm 6.2 \text{ kJ mol}^{-1}$$

* estimated from a post-calorimetric iodide analysis.

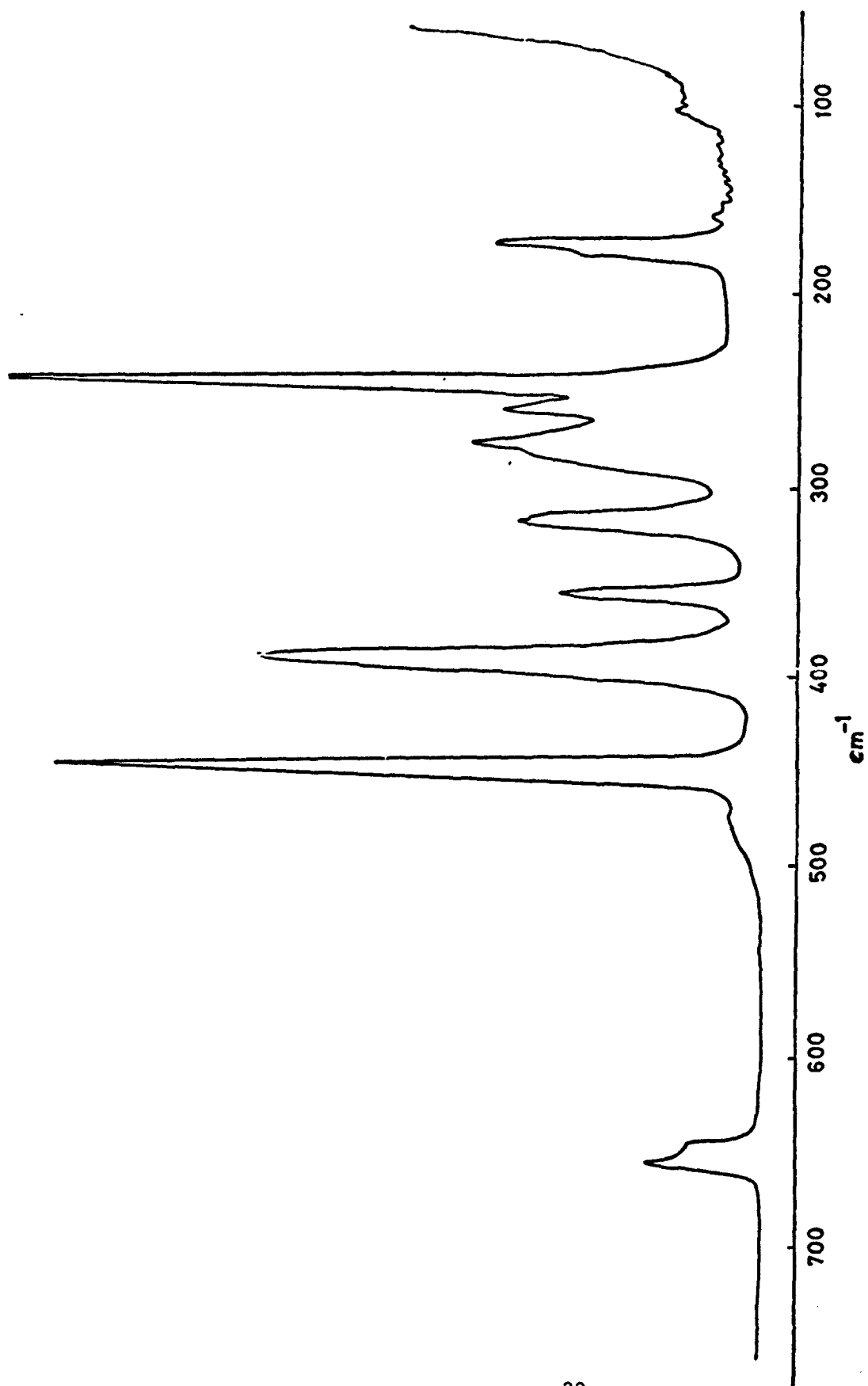


FIGURE 1

RAMAN SPECTRUM OF COMPOUND A

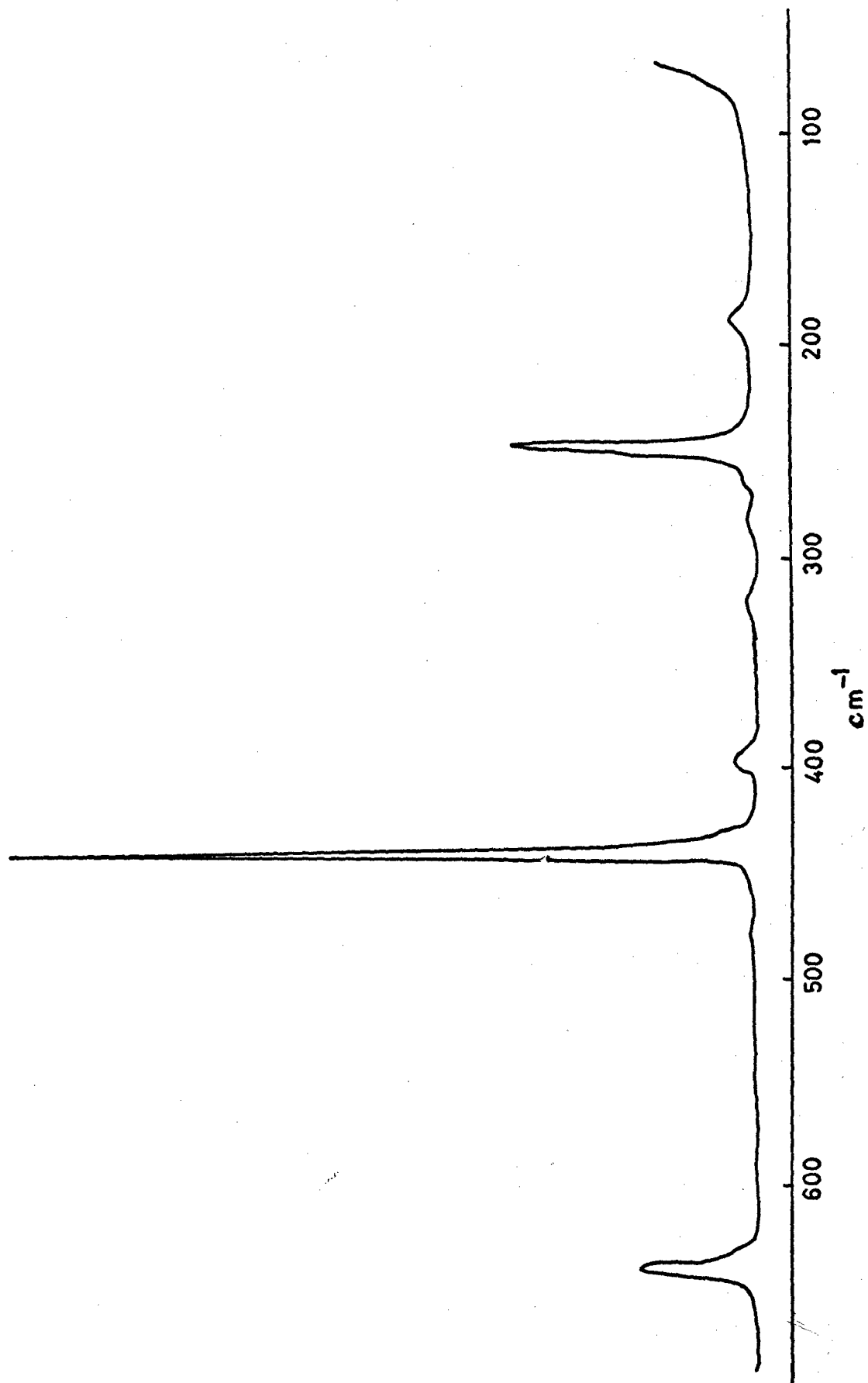


FIGURE 2
RAMAN SPECTRUM OF COMPOUND B

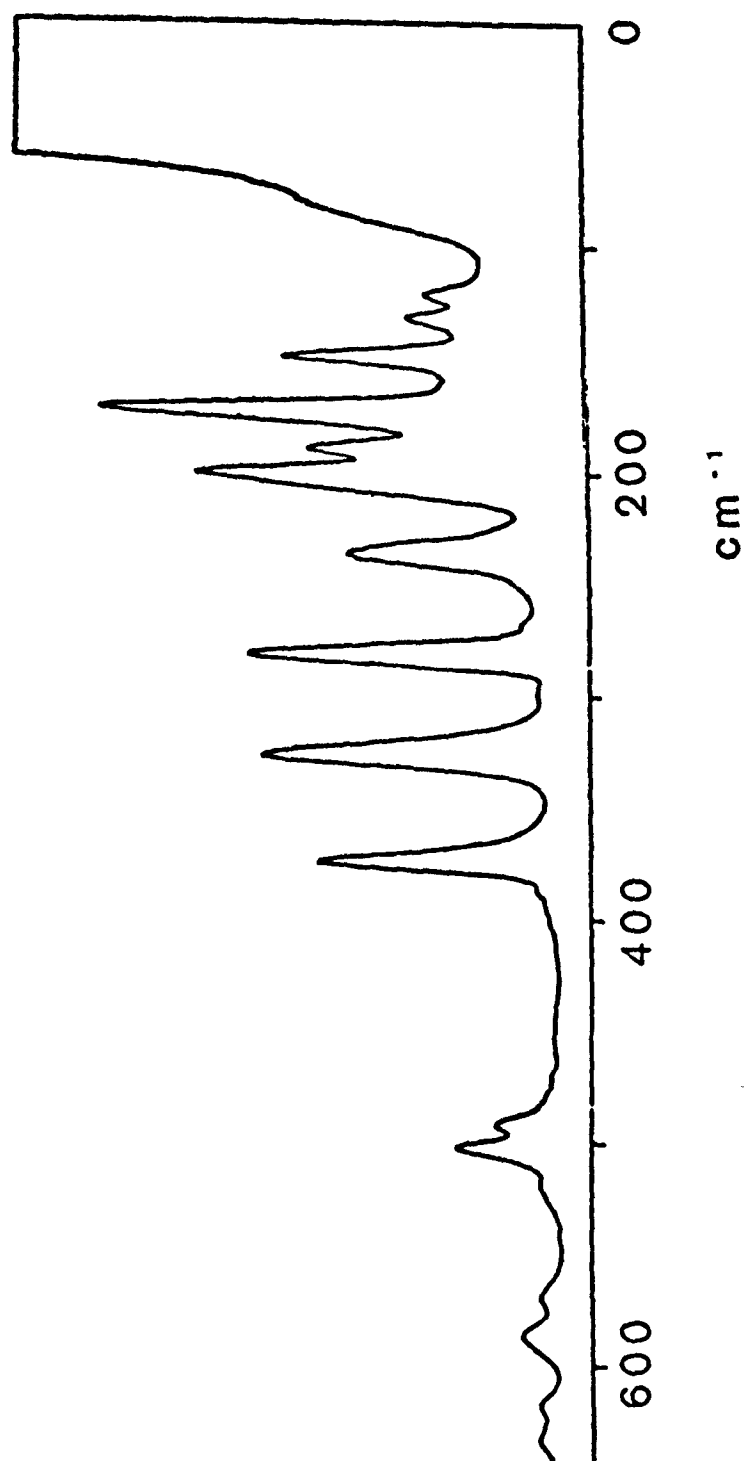


FIGURE 3

RAMAN SPECTRUM OF PRODUCT FROM REACTION OF PCl_2F WITH Br_2

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