Cyano- and Thiocyanato-derivatives of the Hexachlorophosphate Ion (PCl_6^-)

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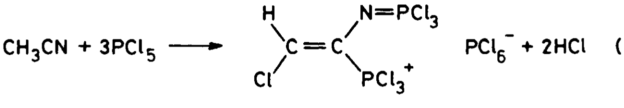
The preparation and identification in solution of several new cyano- and thiocyanato-derivatives of the hexachlorophosphate (PCl_6^-) ion are described. The cyano-complexes $[PCl_{6-n}(CN)_n]^-$ (n = 1—3) and the hexathiocyanatophosphate ion $P(NCS)_6^-$ have been isolated as tetra-n-alkylammonium salts and further characterised by elemental analysis, ^{31}P n.m.r., and (in some cases) vibrational spectroscopy. The *mer* isomer of the $[PCl_3(CN)_3]^-$ ion has been obtained pure and the *fac* isomer in a less pure state (*ca.* 3:1 *fac*:*mer*) by different preparative routes. Isomeric configurations in the chlorothiocyanatophosphate series $[PCl_{6-n}(NCS)_n]^-$ have been assigned on the basis of the pairwise interaction method.

ALTHOUGH many pseudo-halogeno-derivatives of phosphorus, particularly phosphorus(III) compounds, phosphoryl and thiophosphoryl species are known,[1] comparatively little work has been reported on derivatives of the PCl_6^- ion, except for azides.[2-5] The anions $[PCl_{6-n}(CN)_n]^-$ (n = 1 or 2) have been prepared by reaction of PCl_5 with MCN in acetonitrile solution (M = Ag, n = 1 or 2; [6] M = K, n = 2 [7]), but the instability of some of the salts precluded complete characterisation.[6] The formation of six-co-ordinate compounds in these reactions is probably due to the reaction of the metal cyanide with the hexachlorophosphate ion produced by the reaction of PCl_5 with CH_3CN, equation (1).[8] The unstable tetrachlorophosphonium salts reported previously [6] thus probably contain the cation (I) rather than PCl_4^+. The only reports of six-co-ordinate phosphorus(V) anions containing the NCS group are in two recent papers, where the ions $[PF_{6-n}(NCS)_n]^-$ ($1 \leqslant n \leqslant 3$) were identified as products from the reaction of PF_5 with metal thiocyanates.[9] We report some reactions of the PCl_6^- ion with metal cyanides and thiocyanates to yield substituted six-co-ordinate anions containing CN or NCS ligands. The oxidation of some phosphorus(III) derivatives, and ligand exchange reactions between $P(NCS)_3$ or $PO(NCS)_3$ and hexachlorophosphates, have also been shown to lead to new anionic derivatives of phosphorus(V).



$$CH_3CN + 3PCl_5 \longrightarrow (H)(Cl)C{=}C(N{=}PCl_3)(PCl_3^+)\ PCl_6^- + 2HCl \quad (1)$$

(I)

EXPERIMENTAL

All manipulations, including preparation of n.m.r. samples, were carried out under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification except as described below. The NH_4NCS was recrystallised from methanol before use. Tetraethylammonium chloride was dried by heating to 420 K *in vacuo* for 6—7 h, and tetra-n-pentylammonium chloride by heating to 370 K *in vacuo* for 5 h. Anhydrous lithium cyanide was prepared by the method of Ludman [10] from lithium metal and anhydrous HCN, itself obtained by the reaction of KCN with glacial acetic acid. Cyanogen chloride was prepared by the method of Jennings and Scott,[11] and cyanogen by the dry distillation of a mixture of P_2O_5 and oxamide at 423 K. The gas phase i.r. spectra of both products showed only small traces of HCN as impurity. The gas was stored in a rotaflo vessel at 243 K and handled on the vacuum line. The $P(CN)_3$ was prepared by an adaption of the method of Maier.[12] The reflux stage was found to be unnecessary and diethyl ether was preferred as solvent since the silver salts were insoluble in it and it was also easier to remove. The $P(NCS)_3$ was prepared in CH_2Cl_2 solution by adding NH_4NCS in portions to a solution of PBr_3 in this solvent. Vigorous reaction occurred on each addition until all the PBr_3 had reacted. The solution was filtered, stored at 243 K, and used without further purification. Solutions stored at room temperature readily decomposed to insoluble red-brown polymeric materials. The compound $[N(n\text{-}C_5H_{11})_4][PCl_6]$ was prepared as described previously.[5] A relatively simple procedure for the preparation of NEt_4PCl_6 was adopted; PCl_5 was dissolved completely in CH_2Cl_2 and an equimolar amount of NEt_4Cl in the same solvent was added. The reagents must be completely dissolved before mixing, otherwise the insoluble product coats the reactants, preventing complete reaction. The thick white precipitate was filtered off, washed with CH_2Cl_2, and dried *in vacuo* to give a quantitative yield of the hexachlorophosphate. Cyanide residues were destroyed by treatment with 'chloros', a commercially available solution of hypochlorite containing permanganate indicator.

Tetraethylammonium Pentachlorocyanophosphate, $[NEt_4][PCl_5(CN)]$.—Tetra-n-pentylammonium hexachlorophosphate (2.29 g, 6.1 mmol) was dissolved in CH_2Cl_2 and AgCN (0.55 g, 4.1 mmol) added. The solution was stirred for 10 min and filtered. A quantity of NEt_4Cl was added in small portions to the filtrate until its ^{31}P n.m.r. spectrum showed that all the unreacted hexachlorophosphate had precipitated as NEt_4PCl_6; this required approximately 0.16 g. The solution was filtered and NEt_4Cl (0.32 g) added. The small amount of precipitate which resulted was separated; its i.r. spectrum and elemental analysis indicated the presence of $(n\text{-}C_5H_{11})_4N^+$ groups so it was discarded. The filtrate was cooled to 253 K for 2 h, producing white crystals which were separated to give pure $[NEt_4][PCl_5(CN)]$ (0.25 g). On reducing the volume of the filtrate and cooling again to 253 K, a further 0.18 g of product was obtained [Found: C, 29.2; H, 5.7; Cl, 48.7; N, 7.6; P, 8.3. Calc. for $C_9H_{20}Cl_5N_2P$: C, 29.6; H, 5.5; Cl, 48.7; N, 7.7; P, 8.5%].

Tetraethylammonium Tetrachlorodicyanophosphate, $[NEt_4][PCl_4(CN)_2]$.—Powdered NEt_4PCl_6 (3.39 g, 9.1 mmol) was made into a slurry with CH_2Cl_2 (20 cm^3), AgCN (1.15 g, 8.6 mmol) was added, and the mixture stirred for 20 h. The solution was filtered and the remaining solid extracted several times with CH_2Cl_2. The filtrate and washings were combined and reduced in volume until crystallisation became apparent; the solution was then cooled to 253 K. The long needle-like crystals were separated and dried *in vacuo* to give $[NEt_4][PCl_4(CN)_2]$ as an isomeric mixture (0.67 g). Treatment of the remaining solution with light petroleum (b.p. 30—40 °C) precipitated a further 0.32 g of product [Found: C, 32.4; H, 5.6; Cl, 42.0; N, 12.2; P, 9.5. Calc. for $C_{10}H_{20}Cl_4N_3P$: C, 33.8; H, 5.6; Cl, 40.0; N, 11.8; P, 8.7%].

Tetraethylammonium Trichlorotricyanophosphate, $[NEt_4][PCl_3(CN)_3]$ (Mer *Isomer*).—Powdered NEt_4PCl_6 (3.48 g, 9.3 mmol) was made into a slurry with CH_2Cl_2 (20 cm^3), AgCN (5.48 g, 43.6 mmol) was added, and the mixture stirred for 20 h. The solution was filtered and the silver residues extracted several times with CH_2Cl_2. The combined filtrate and washings were reduced in volume until recrystallisation started, when the solution was cooled to 253 K. The resulting crystals were separated to give $[NEt_4][PCl_3(CN)_3]$ (1.01 g) as an isomer mixture containing a *ca.* 10 : 1 ratio of the *mer* : *fac* isomers, as estimated by ^{31}P n.m.r. Further extraction of the solid residues with CH_2Cl_2 followed by treatment of the washings with light petroleum (b.p. 30—40 °C) gave another 0.48 g of product. The pure *mer* isomer was obtained by recrystallising twice from CH_2Cl_2 [Found: C, 39.0; H, 6.3; Cl, 30.7; N, 15.9; P, 9.2. Calc. for $C_{11}H_{20}Cl_3N_4P$: C, 38.2; H, 5.8; Cl, 30.8; N, 16.2; P, 9.0%].

Tetraethylammonium Trichlorotricyanophosphate, $[NEt_4][PCl_3(CN)_3]$ (3 : 1 Fac : Mer *Ratio*).—Compounds $P(CN)_3$ (1.51 g, 13.9 mmol) and NEt_4Cl (2.51 g, 15.2 mmol) were dissolved in CH_2Cl_2, and Cl_2 (0.6 cm^3 at 194 K) was condensed onto the solution frozen in liquid nitrogen under vacuum. The mixture was warmed to 194 K until the green colour disappeared. The solution was then evaporated and the resulting solid recrystallised from CH_2Cl_2 to give $[NEt_4][PCl_3(CN)_3]$ (0.8 g) with a *fac* : *mer* ratio of *ca.* 3 : 1 as estimated by ^{31}P n.m.r. [Found: C, 38.6; H, 5.8; Cl, 32.5; N, 15.8; P, 8.1%].

Tetraethylammonium Dichlorotetracyanophosphate, $[NEt_4][PCl_2(CN)_4]$.—The n.m.r. spectrum of the filtrate from the first recrystallisation in the preparation of *mer*-$[NEt_4][PCl_3(CN)_3]$ above showed the presence of another six-coordinate phosphorus species [$\delta(^{31}P)$ -356.2 p.p.m.]. The filtrate was reduced in volume and cooled to 253 K to precipitate as much as possible of the remaining $[NEt_4][PCl_3(CN)_3]$. The crystals were separated and the filtrate retained. This process was repeated twice. The solution was then evaporated and the resultant solid analysed [Found: C, 41.2; H, 7.4; N, 18.9. Calc. for $C_{12}H_{20}Cl_2N_5P$: C, 42.9; H, 6.0; N, 20.8%]. Insufficient solid was available for phosphorus or chlorine analyses, or for further repeating the purification procedure. The product was thus mainly $[NEt_4][PCl_2(CN)_4]$, contaminated by a small amount of $[NEt_4][PCl_3(CN)_3]$, as confirmed by ^{31}P n.m.r. spectroscopy.

Tetra-n-pentylammonium Hexathiocyanatophosphate, $[N(n\text{-}C_5H_{11})_4][P(NCS)_6]$.—The compound $[N(n\text{-}C_5H_{11})_4][PCl_6]$ (3 g, 5.5 mmol) was treated with a large excess of NH_4NCS in CH_2Cl_2 (50 cm^3). The mixture was stirred for 10 min and filtered. The resultant yellow solution was evaporated under vacuum, care being taken not to heat the flask too strongly in order to avoid decomposition of the $P(NCS)_6^-$ ion. The product was an intractable orange oil [Found: C, 45.0; H, 7.9; N, 11.6; P, 4.6; S, 25.0. Calc. for $C_{26}H_{44}N_7PS_6$: C, 46.1; H, 6.5; N, 14.5; P, 4.6; S, 28.4%]. Attempted recrystallisation at 194 K failed, and no further purification was possible due to the thermally unstable nature of the compound, probably involving loss of CS_2 (see Results and Discussion section) which could account for the low sulphur analysis. The compound was heated for 5 h at 373 K *in vacuo* and the product analysed [Found: C, 48.0; H, 6.9; N, 15.3; S, 25.0. Calc. for $2[N(n\text{-}C_5H_{11})_4][P(NCS)_6] - CS_2$: C, 47.9; H, 7.6; N, 13.7; S, 25.0%].

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on the Fourier transform spectrometer as described previously,[5] using stationary sample tubes of 8.4 mm outside diameter. Chemical shifts were measured relative to external H_3PO_4, and are quoted with the downfield direction taken as positive. The C, H, N, P, and Cl microanalyses were obtained as described in earlier papers.[13] Infrared spectra were recorded on a Perkin-Elmer 457 instrument, either as Nujol mulls on CsI plates, protected by Polythene discs where necessary, or as solutions in the appropriate solvent. Raman spectra were recorded by Mrs. J. Slegrova on a Cary 82 spectrometer using an argon laser.

RESULTS AND DISCUSSION

(1) *Chlorocyanophosphates.*—(*a*) *Preparation by direct substitution into the hexachlorophosphate ion.* Silver(I) cyanide was found to be the most effective reagent for introducing cyano-groups into the PCl_6^- ion. The reactions were rapid and no phosphorus(III) by-products were formed. With $Zn(CN)_2$ the formation of PCl_3, in addition to $[PCl_{6-n}(CN)_n]^-$ species, was observed. Both KCN and NaCN did not react with the hexachlorophosphate ion in CH_2Cl_2 and LiCN reacted only very slowly.

By reaction of known ratios of $[N(n\text{-}C_5H_{11})_4][PCl_6]$ to AgCN in CH_2Cl_2 and observation of the resulting ^{31}P n.m.r. spectra, assignments of chemical shifts to the substituted anions $[PCl_{6-n}(CN)_n]^-$ (n = 1—3) could be made (Table 1). The two possible isomers of both $[PCl_4(CN)_2]^-$ and $[PCl_3(CN)_3]^-$ were detected, but one was present in higher concentration in each case. The assignment of peaks to specific isomers is discussed below [section (*c*)]. A 1 : 1 ratio of PCl_6^- : AgCN afforded both unreacted PCl_6^- and $[PCl_4(CN)_2]^-$ as well as the major product $[PCl_5(CN)]^-$; similarly a 1 : 2 ratio of reactants gave $[PCl_5(CN)]^-$ and $[PCl_3(CN)_3]^-$ in addition to $[PCl_4(CN)_2]^-$. With 1 : 4 and 1 : 6 ratios of PCl_6^- to AgCN, only the two isomers of $[PCl_3(CN)_3]^-$ were formed.

TABLE 1

Values of $\delta(^{31}P)$ (p.p.m.) for $[PCl_{6-n}(CN)_n]^-$ ions in CH_2Cl_2

n	0	1	2		3	
$\delta(^{31}P)$	-298.2	-309.5	-315.0	-331.2 *	-340.0 *	-351.2

* More abundant isomer.

The reaction of a slurry of NEt_4PCl_6 with AgCN in CH_2Cl_2 gave rise to soluble products, apart from $[NEt_4][PCl_5(CN)]$, and allowed the isolation of the individual compounds (Experimental section). Thus $[PCl_3(CN)_3]^-$, prepared as its NEt_4^+ salt and initially isolated as a *ca.* 10 : 1 mixture of the two possible isomers, was recrystallised, giving the *mer* isomer (δ − 340.0 p.p.m.), the crystal structure of which has very recently been determined.[14] The compound $[NEt_4][PCl_4(CN)_2]$ was also isolated, but the presence of both isomers (the isolation procedure increased the relative concentration of the initially less abundant isomer) in the solid precluded structural assignments on the basis of vibrational spectra. The vibrational spectra of $[NEt_4][PCl_5(CN)]$ were consistent with the expected C_{4v} symmetry. Solid state ^{31}P n.m.r. spectra were recorded for each compound and gave chemical shifts in good agreement with the solution values. Separate signals could not be resolved, however, from *cis*- and *trans*-$[PCl_4(CN)_2]^-$.

(*b*) *Preparation by oxidation of phosphorus*(III) *compounds.* The reaction between equimolar quantities of $P(CN)_3$, NEt_4Cl, and Cl_2 in CH_2Cl_2 afforded a *ca.* 3 : 1 mixture of *fac* : *mer* $[PCl_3(CN)_3]^-$,[14] together with some $[PCl_2(CN)_2]^-$ (δ − 154.7 p.p.m.).[15] The preferential formation of *fac*-$[PCl_3(CN)_3]^-$ in this oxidation reaction is entirely compatible with the geometry of the starting material $[PCl(CN)_3]^-$, which has a pseudo-facial arrangement of cyano-groups.[16] Attempts to prepare highly substituted cyano-containing anions by the oxidation of $[PCl(CN)_3]^-$ with ClCN or $(CN)_2$ failed to produce any six-co-ordinate species.

The reaction of $[NEt_4][PCl(CN)_3]$ with Br_2 in CH_2Cl_2 was violently exothermic. The ^{31}P n.m.r. spectrum showed phosphorus(III) chlorobromides, predominantly PBr_3 as the main product, together with four resonances in the six-co-ordinate region at −338.4 (*mer*-$[PCl_3(CN)_3]^-$), −398.0, −417.2, and −440.0 p.p.m. The signals to lower frequency of *mer*-$[PCl_3(CN)_3]^-$ rapidly diminished in intensity, with a corresponding increase in the concentration of PBr_3. The main reaction is clearly ligand exchange between $[PCl(CN)_3]^-$, which is in a dynamic equilibrium [equation (2)], and bromine,

$$[PCl(CN)_3]^- \rightleftharpoons P(CN)_3 + Cl^- \qquad (2)$$

although some oxidation to give bromine-containing anions is indicated. In the presence of excess NEt_4Cl to suppress the dissociation of $[PCl(CN)_3]^-$, an exothermic reaction again occurred. The n.m.r. spectrum showed no phosphorus(III) species in solution, but a major resonance at −440.0 p.p.m., assigned as an isomer of $[PClBr_2(CN)_3]^-$, with lower intensity signals due to the isomers of $[PCl_4(CN)_2]^-$ (mainly *trans*) and $[PCl_3(CN)_3]^-$ (mainly *mer*). The bromine-containing anion decomposed over a period of 2 d, the main products being $[PCl_2(CN)_2]^-$ (δ − 153.1 p.p.m.)[15] and *trans*-$[PCl_4(CN)_2]^-$, with smaller peaks present due to PCl_3, *cis*-$[PCl_4(CN)_2]^-$, both isomers of $[PCl_3(CN)_3]^-$, and at −9.8 (unassigned), −373.9, and −398.0 p.p.m., the latter two probably from isomers of $[PCl_2Br(CN)_3]^-$. One day after sample preparation $[PCl_5(CN)]^-$ was also present, but this did not appear in the spectrum on the following day. Attempts to isolate $[NEt_4][PClBr_2(CN)_3]$ by adding bromine dropwise to a solution of $[NEt_4][PCl(CN)_3]$ containing excess NEt_4Cl until a slight bromine colouration persisted, and removal of the solvent *in vacuo*, led only to the formation of *fac*-$[PCl_3(CN)_3]^-$ [$\delta(^{31}P)$ − 352 p.p.m.] as the major component of the solid, together with smaller quantities of the *mer* isomer and $[PCl_4(CN)_2]^-$, mainly the *cis* isomer. The preferential formation of *fac*-$[PCl_3(CN)_3]^-$ in this reaction strongly suggests that the cyanide ligands may have a facial arrangement in the predominant isomer of $[PClBr_2(CN)_3]^-$, which would again be in keeping with the structure of $[PCl(CN)_3]^-$.[16]

A similar reaction but using $N(n\text{-}C_3H_7)_4Br$ to suppress the dissociation of the $[PCl(CN)_3]^-$ ion gave PBr_3 as the most intense peak, although high field resonances at −398.0, −417.5, and −440.0 p.p.m. were again apparent. The oxidation of $[N(n\text{-}C_3H_7)_4][PBr(CN)_3]^-$ [15,17,18] with chlorine in the presence of $N(n\text{-}C_3H_7)_4Br$ led to the formation of approximately equal amounts of *fac*- and *mer*-$[PCl_3(CN)_3]^-$, together with a stronger ^{31}P resonance at −441.5 p.p.m., ascribed to *fac*-$[PClBr_2(CN)_3]^-$. Over a 2 d period the signals for $[PCl_3(CN)_3]^-$ increased in relative intensity, and small resonances due to the isomers of $[PCl_4(CN)_2]^-$ became apparent, together with a signal at −399.7 p.p.m. No decomposition to phosphorus(III) species was observed. Degradation of the bromo-anions in this system occurred very slowly, and signals at −399.7 and −441.5 p.p.m. could still be detected after 1 year, although they were much reduced in intensity.

A signal between −398.0 and −399.7 p.p.m. is thus observed in many systems, and is almost certainly due to an isomer of $[PCl_2Br(CN)_3]^-$, probably the *fac* isomer if the assignment for $[PClBr_2(CN)_3]^-$ is correct, formed by substitution by excess Cl^- into the latter. The resonance sometimes seen at −417.2 or −417.5 p.p.m. is probably from one of the two possible *mer* isomers of $[PClBr_2(CN)_3]^-$, and the signal at −373.9 p.p.m. seen in one of the systems could arise from a *mer* isomer of $[PCl_2Br(CN)_3]^-$, but unambiguous assignment is not possible.

Attempted preparation of $[PCl_2Br_2(CN)_2]^-$ by oxidation of $[PCl_2(CN)_2]^-$ [15] with bromine in the presence of NEt_4Cl gave PCl_3 as the chief product, together with $[PCl_5(CN)]^-$ and the isomers of $[PCl_4(CN)_2]^-$ (mainly *trans*). Similarly the attempted oxidation of $[PBr_2(CN)_2]^-$ [17,18] with Cl_2 in the presence of NEt_4Br, using $CHCl_3$ as solvent, gave approximately equal amounts of the isomers of $[PCl_4(CN)_2]^-$ and a small quantity of $[PCl_5(CN)]^-$. Small unassigned peaks at 4.9 p.p.m. were also observed in both instances. Attempts to prepare $[PBr_3(CN)_3]^-$ by bromine oxidation of $[PBr(CN)_3]^-$ [18,19] yielded only PBr_3.

A reasonable rationalisation for the products in the above oxidation reactions is that direct halogen oxidation of a species such as $[PCl(CN)_3]^-$ [16] or $[PBr(CN)_3]^-$ [17–19] with a pseudo-facial arrangement of cyano-groups leads predominantly to *fac* isomers of $[PCl_nBr_{3-n}(CN)_3]^-$ ions (n = 1—3), whereas if the starting material is $[PCl_2(CN)_2]^-$ [15] or $[PBr_2(CN)_2]^-$ [18] both isomers of $[PCl_4(CN)_2]^-$ are formed, even though the two CN groups occupy equatorial positions in the ψ-trigonal bipyramidal structure of $[PBr_2(CN)_2]^-$.[18] Since $[PCl_2(CN)_2]^-$ was detected in the decomposition products from $[PClBr_2(CN)_3]^-$, oxidation of this species could account for the formation of both isomers of $[PCl_4(CN)_2]^-$ in the $[PCl(CN)_3]^-$–Br_2 reaction. No evidence was found for six-co-ordinate species containing more than two bromine atoms, and more highly brominated species appear to be intrinsically unstable under the experimental conditions with respect to elimination of a pseudo-halogen such as $(CN)_2$ or CNCl and formation of PBr_3.

(*c*) *Structures and properties of the chlorocyanophosphates.* As mentioned above, the crystal structure of *mer*-$[PCl_3(CN)_3]^-$ (as its NEt_4^+ salt) has been determined very recently,[14] and this is now known to be the more abundant isomer in the substitution reactions [$\delta(^{31}P)$ −340.0 p.p.m.]. The crystals obtained by chlorine oxidation of $[NEt_4][PCl(CN)_3]$ have similarly been shown to contain mainly the *fac* isomer.[14] In principle these ions are distinguishable by vibrational spectroscopy, since the *fac* isomer is expected to show 14 fundamental bands in both the i.r. and Raman spectra, whereas the *mer* isomer should give more complex spectra with 22 i.r. and 24 Raman bands. In practice the spectra appeared to be more complex from the *fac* isomer with 15 bands observed in the i.r. and 14 in the Raman spectrum between 4 000 and 250 cm^{-1}, while the *mer* isomer showed only 11 bands in the i.r. and 14 in the Raman spectrum. Indeed the isomers were originally wrongly assigned on the basis of their vibrational spectra. There remains the assignment of structures to the two isomers of $[PCl_4(CN)_2]^-$ detected by ^{31}P n.m.r. spectroscopy, and to the one isomer seen for $[PCl_2(CN)_4]^-$, as mentioned below. This is possible on the basis of the pairwise interaction method,[20-24] which has previously been applied successfully to the azidochlorophosphates.[4,5]

As a first approximation the Cl : Cl term was taken as −24.85 p.p.m. from PCl_6^-, the CN : Cl term as −27.68 p.p.m. from $[PCl_5(CN)]^-$, and the CN : CN term as the weighted average (−35.89 p.p.m.) from *mer*- and *fac*-$[PCl_3(CN)_3]^-$, which are the known structures in the series. The shifts calculated for the two possible isomers of both $[PCl_4(CN)_2]^-$ and $[PCl_2(CN)_4]^-$ from these data are shown in column (A) of Table 2. Although the agreement between calculated and experimental values is only moderate, the results suggest that the *cis* isomer of $[PCl_4(CN)_2]^-$ is the more abundant [δ (^{31}P) −331.2 p.p.m.] and that the single isomer observed for $[PCl_2(CN)_4]^-$ probably has a *trans* structure. Statistically the *cis* isomer of $[PCl_4(CN)_2]^-$ is four times more likely than the *trans* isomer to be formed by substitution into $[PCl_5(CN)]^-$ if there are no directive effects from the substituents already present, so the assignment of this as the more abundant isomer does not appear unreasonable. In practice the intensity ratio was less than 4 : 1 for the signals at −331.2 and −315.0 p.p.m., so the presence of the cyano-group in $[PCl_5(CN)]^-$ may exert some directive influence in favour of substitution *trans* to itself, in keeping with the greater *trans* effect of cyanide than chloride in square planar complexes.[25]

TABLE 2

Calculated and observed shifts for $[PCl_{6-n}(CN)_n]^-$ (n = 0—4) ions

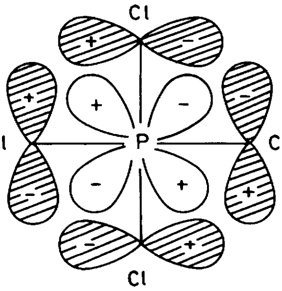
Ion	Calculated shift		$\delta(^{31}P)$/ p.p.m.
	(A)	(B)	
PCl_6^-			−298.2
$[PCl_5(CN)]^-$		−307.6	−309.5
trans-$[PCl_4(CN)_2]^-$	−320.8	−316.9	−315.0
cis-$[PCl_4(CN)_2]^-$	−326.2	−324.3	−331.2
mer-$[PCl_3(CN)_3]^-$	−342.9	−341.0	−340.0
fac-$[PCl_3(CN)_3]^-$	−348.3	−348.3	−351.2
trans-$[PCl_2(CN)_4]^-$	−365.0	−365.0	−356.2
cis-$[PCl_2(CN)_4]^-$	−370.4	−372.4	

The pairwise interaction terms were refined by taking these suggested assignments as correct, deriving the CN : Cl term (−27.19 p.p.m.) as the weighted average from $[PCl_5(CN)]^-$ and *trans*-$[PCl_4(CN)_2]^-$, and the CN : CN term (−36.88 p.p.m.) as the weighted average from *cis*-$[PCl_4(CN)_2]^-$, *mer*-$[PCl_3(CN)_3]^-$, *fac*-$[PCl_3(CN)_3]^-$, and *trans*-$[PCl_2(CN)_4]^-$; the results are shown in column (B) of Table 2. The larger than expected deviations, particularly for *cis*-$[PCl_4(CN)_2]^-$ and *trans*-$[PCl_2(CN)_4]^-$, may possibly arise from distortion of the octahedron, since the method assumes that the co-ordination polyhedron retains a regular geometry throughout. Nevertheless the pattern of substitution seems to be satisfactorily established.

As previously observed,[7] the $[PCl_4(CN)_2]^-$ ion is only slowly hydrolysed by atmospheric moisture, in marked contrast with the hexachlorophosphate ion. Thus a sample of the solid when redissolved in CH_2Cl_2 after overnight exposure to the laboratory atmosphere showed the bulk of the material to be unchanged. Small resonances were observed at 0.0, −14.5, −29.1, and −53.3 p.p.m. tentatively assigned as $P(O)Cl_{3-n}(CN)_n$ (n = 0—3). Either an unassigned doublet [δ −33.1 p.p.m., J(PH) 355 Hz], or two equally intense singlets at −25.8 and −40.4 p.p.m., were also present. The $[PCl_4(CN)_2]^-$ ions were inert to further substitution by ligands other than CN^-, and reaction with LiN_3 [26] gave no evidence of the formation of $[PCl_3(CN)_2(N_3)]^-$.

Both isomers of $[NEt_4][PCl_3(CN)_3]$ are even more stable, showing no sign of hydrolysis after exposure for several months to the atmosphere. Reagents which readily substitute the PCl_6^- ion such as LiN_3 [4,5] or NH_4NCS (this work) do not react with the $[PCl_3(CN)_3]^-$ ion. The only evidence of further substitution was the observation of a resonance at −356.2 p.p.m. in the ^{31}P n.m.r. spectrum from a reaction between NEt_4PCl_6 and excess AgCN, used to prepare *mer*-$[PCl_3(CN)_3]^-$. Although the species giving rise to this peak could not be obtained uncontaminated by $[NEt_4][PCl_3(CN)_3]$, the elemental analysis indicated that the $[PCl_2(CN)_4]^-$ ion was present. Unfortunately the preparation of this ion was not reproducible and the exact conditions for its formation are unclear. It has been assigned a *trans* structure on the basis of the pairwise interaction calculations described above.

The stability towards both further substitution and hydrolysis of these ions indicates a marked strengthening of the P–Cl bonds in $[PCl_3(CN)_3]^-$ over those in related ions such as $[PCl_3(N_3)_3]^-$ [4,5] and $[PCl_3(NCS)_3]^-$. This difference between cyanide and other ligands is readily explicable in terms of simple ligand field theory. As the CN group is the highest in the spectrochemical series [27] of all the common ligands, the separation between the t_{2g} and $e_g{}^*$ orbitals in the complex is expected to be larger than that produced by ligands which give lower Δ values such as F, NCS, or N_3. This could lead to a lowering in energy of the unoccupied 3d t_{2g} orbitals on phosphorus and hence to P–Cl π-bonding by donation from filled orbitals on Cl, as shown in the Figure. The more CN groups incorporated into the complex the stronger the P–Cl π-bonding should be, and in $[PCl_3(CN)_3]^-$ the P–Cl bonds are sufficiently strengthened to resist further substitution. A similar rationalisation is proposed to account for the lack of reaction between $[PCl_4(bipy)]^+$ (bipy = 2,2′-bipyridyl) and LiN_3,[28] where bipy is also quite high in the spectrochemical series, since the cations $[PCl_{4-n}(N_3)_n(bipy)]^+$ ($0 \leqslant n \leqslant 4$) are stable and readily prepared by an alternative route.[28] In this case the charge on the complex may also contribute to the strengthening of the P–Cl bonds.



Possible P–Cl π-bonding in chlorocyanophosphates

The degree of substitution attainable in six-co-ordinate phosphorus complexes thus seems to depend on the position of the ligand(s) in the spectrochemical series. Ligands with low Δ values can form PX_6^- ions from PCl_6^-, *e.g.* X = F, N_3, or NCS, whereas the presence of ligands with high Δ values renders the remaining P–Cl bonds relatively inert towards further substitution.

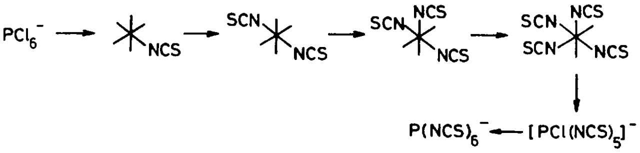
(2) *Chlorothiocyanatophosphates*.—(*a*) *Preparation by direct substitution into the hexachlorophosphate ion*. The reaction of $[N(n\text{-}C_5H_{11})_4][PCl_6]$ with MNCS (M = Ag, Li, or NH_4) in CH_2Cl_2 solution was rapid. With excess thiocyanate the fully substituted $P(NCS)_6^-$ anion was formed, giving a ^{31}P n.m.r. signal in solution at −261.9 p.p.m. The compound $[N(n\text{-}C_5H_{11})_4][P(NCS)_6]$ was isolated as an intractable orange oil. The i.r. spectrum of a freshly prepared sample showed strong absorptions at 2 040 and 1 900 cm^{-1}, indicating that the ligand is *N*- rather than *S*-bonded.[29] The complex is thermally unstable, decomposing at room temperature to give CS_2 (identified by its gas phase i.r. spectrum), and a polymeric solid which gave a broad solid state ^{31}P n.m.r. signal of some 4 kHz width centred at 0 p.p.m., with no discernible maxima. This suggests that the solid contains phosphorus atoms in several different environments. The compound was considerably more stable at 243 K, however. The ^{31}P n.m.r. spectrum of the liquid consisted of a single sharp resonance at −261.1 p.p.m., in excellent agreement with the solution value.

With smaller quantities of MNCS the $[PCl_{6-n}(NCS)_n]^-$ species could be observed in solution (Table 3). Only one of the possible isomers where n = 2—4 was detected in each case. The substitution reaction was accompanied by the rapid reduction of phosphorus(V) derivatives to give PCl_3. The chlorothiocyanatophosphates rapidly decomposed to PCl_3 and $P(S)Cl_3$ (δ 34 p.p.m.). Assignments of chemical shifts to $[PCl_5(NCS)]^-$ and $P(NCS)_6^-$ are unambiguous, thus enabling the chemical shifts of the isomers of $[PCl_{6-n}(NCS)_n]^-$ ($2 \leqslant n \leqslant 5$) to be calculated on the basis of the pairwise interaction method.[20-24] The values obtained are shown in column (A) of Table 3 and give best agreement if the pattern of substitution indicated in the Scheme is followed, *i.e.* *trans*, *mer*, *cis* for n = 2, 3, and 4 respectively. The pairwise interaction parameters were refined by a least-squares method, and the best fit values obtained were Cl : Cl −24.83, Cl : NCS −22.13, and NCS : NCS −21.81 p.p.m. The chemical shifts recalculated from these data are shown in column (B) of Table 3. The agreement between experimental and calculated values is in general very good. It is interesting to note that substitution does not follow the *cis-fac-cis* pattern which has been deduced previously for $[PF_{6-n}Cl_n]^-$,[30] $[PCl_{6-n}(N_3)_n]^-$,[4,5] and $[SbCl_{6-n}Br_n]^-$.[24] The same sequence has also been proposed for $[NbCl_{6-n}Br_n]^-$,[23] but this conclusion has been disputed and the alternative sequence *cis-mer-cis* suggested for the more abundant isomers.[31] The latter pattern, which accords with statistical predictions for substitution or ligand exchange reactions, is ob-

TABLE 3

Calculated and observed shifts for $[PCl_{6-n}(NCS)_n]^-$ (n = 0—6) ions

Ion	Calculated shift (A)	Calculated shift (B)	δ(^{31}P)/ p.p.m.
PCl_6^-		−298.0	−298.2
$[PCl_5(NCS)]^-$		−287.2	−286.9
trans-$[PCl_4(NCS)_2]^-$	−275.6	−276.4	−276.1
cis-$[PCl_4(NCS)_2]^-$	−278.3	−278.7	
mer-$[PCl_3(NCS)_3]^-$	−269.6	−270.3	−270.5
fac-$[PCl_3(NCS)_3]^-$	−272.2	−272.7	
trans-$[PCl_2(NCS)_4]^-$	−263.2	−264.3	
cis-$[PCl_2(NCS)_4]^-$	−266.2	−266.9	−266.8
$[PCl(NCS)_5]^-$	−262.8	−263.0	−264.4
$P(NCS)_6^-$		−261.7	−261.9



SCHEME The suggested pattern of substitution in the $[PCl_{6-n}(NCS)_n]^-$ series served for $[SnCl_{6-n}Br_n]^{2-}$, although all the possible isomers are present.[32]

(*b*) *Preparation by ligand redistribution reactions.* When small quantities of $P(NCS)_3$ or $PO(NCS)_3$ were added to concentrated solutions of $[N(n\text{-}C_5H_{11})_4][PCl_6]$ rapid ligand redistribution occurred, giving $[PCl_{3-n}(NCS)_n]$ or $P(O)Cl_{3-n}(NCS)_n$ $(0 \leqslant n \leqslant 3)$,[1] together with the $[PCl_{6-n}(NCS)_n]^-$ series. The single isomers detected for the bis-, tris-, and tetrakis-thiocyanato-complexes had identical shifts and hence the same *trans*, *mer*, and *cis* structures deduced for the products of the direct substitution reaction.

The anion NCS^- is much lower in the spectrochemical series than CN^-,[27] and as expected substitution is facile in this series right up to $P(NCS)_6^-$. In contrast with the cyanides, there is clearly no particular stability associated with a structure such as $[PCl_3(NCS)_3]^-$.

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REFERENCES

[1] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.

[2] H. W. Roesky, *Angew. Chem. Int. Ed. Engl.*, 1967, **6**, 637.

[3] P. Volgnandt and A. Schmidt, *Z. Anorg. Allg. Chem.*, 1976, **425**, 189.

[4] K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Chem. Commun.*, 1979, 889.

[5] K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1980, 1036.

[6] J. F. Walther, M.Sc. thesis, Ohio State University, 1963.

[7] H. W. Roesky, *Angew. Chem. Int. Ed. Engl.*, 1967, **6**, 363.

[8] H. P. Latscha, W. Weber, and M. Becke-Goehring, *Z. Anorg. Allg. Chem.*, 1969, **367**, 40.

[9] E. G. Il'in, A. P. Nazarov, M. N. Shcherbakova, and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 1980, **250**, 367; P. J. Chevrier and S. Brownstein, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1397.

[10] H. D. B. Jenkins, K. F. Pratt, and T. C. Waddington, *J. Inorg. Nucl. Chem.*, 1977, **39**, 213.

[11] W. L. Jennings and W. B. Scott, *J. Am. Chem. Soc.*, 1919, **41**, 1241.

[12] L. Maier, *Helv. Chim. Acta*, 1963, **46**, 2667.

[13] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1977, 1410.

[14] W. S. Sheldrick, K. B. Dillon, and A. W. G. Platt, unpublished work.

[15] A. W. G. Platt, Ph.D. thesis, Durham, 1980.

[16] W. S. Sheldrick, A. Schmidpeter, F. Zwaschka, K. B. Dillon, and A. W. G. Platt, *Z. Anorg. Allg. Chem.*, submitted for publication.

[17] A. Schmidpeter and F. Zwaschka, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 411.

[18] W. S. Sheldrick, A. Schmidpeter, F. Zwaschka, K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1981, 413.

[19] W. S. Sheldrick, F. Zwaschka, and A. Schmidpeter, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 935.

[20] T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 1967, **46**, 1830.

[21] J. S. Hartman and J. M. Miller, *Inorg. Chem.*, 1974, **13**, 1467.

[22] K. B. Dillon and J. M. Miller, unpublished work.

[23] R. G. Kidd and H. G. Spinney, *Inorg. Chem.*, 1973, **12**, 1967.

[24] R. G. Kidd and H. G. Spinney, paper presented at 5th Int. Conf. on Non-Aqueous Solutions, Leeds, 1976.

[25] D. E. Clegg, J. R. Hall, and G. A. Swile, *J. Organomet. Chem.*, 1972, **38**, 403.

[26] N. Hofmann-Bang, *Acta Chem. Scand.*, 1957, **11**, 581.

[27] C. K. Jørgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.

[28] K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1981, 2292.

[29] K. Oba, F. Watari, and K. Aida, *Spectrochim. Acta, Part A*, 1967, **23**, 1515.

[30] E. G. Il'in, M. N. Shcherbakova, and Yu. A. Buslaev, *Koord. Khim.*, 1975, **1**, 989.

[31] V. P. Tarasov, V. I. Privalov, and Yu. A. Buslaev, *Mol. Phys.*, 1978, **35**, 1047.

[32] K. B. Dillon and A. Marshall, unpublished work.