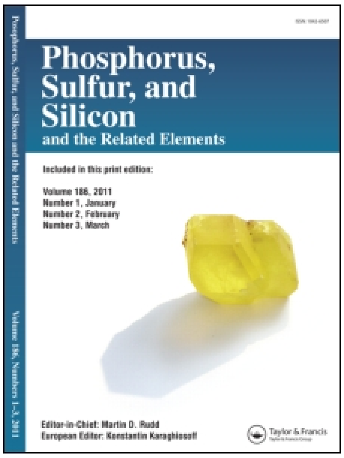

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N- AND O-BONDED CYANATO-DERIVATIVES OF THE HEXACHLOROPHOSPHATE $[PCl_6]^-$ ION

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^{31}P n.m.r. spectroscopy has led to the identification in solution of several ions in the series $[PCl_{6-n}(NCO)_n]^-$ and $[PCl_{6-n}(OCN)_n]^-$, which were obtained by different preparative routes; isomeric configurations have been assigned by the method of pairwise interactions from the observed chemical shifts. The complexes are all unstable, and decompose readily at room temperature.

INTRODUCTION

^{31}P n.m.r. spectroscopy is a valuable technique for the identification of pseudohalogeno-phosphorus species in solution, as shown by literature data,[1,2] but most results are for phosphorus(III), phosphoryl or thiophosphoryl compounds. Less has been published about six-coordinate phosphorus(V) derivatives; some fluoro-anions with azide, cyanide or thiocyanate ligands present have been reported,[3,4] and shift data for azido-, cyano- and thiocyanato-derivatives of PCl_6^- [5–8] and some chlorofluorophosphate[9,10] ions have been given recently. The thiocyanato-complexes were deduced to be N- rather than S-bonded from n.m.r.[3] or vibrational[8] spectroscopy, indicating that phosphorus(V) behaves as a hard acid in these systems. No cyanato-complexes of six-coordinate phosphorus have been described, however. There are clearly possibilities of obtaining linkage (N- or O-bonded) isomers with the cyanate ligand, since both of its possible coordination sites are hard bases. We present ^{31}P n.m.r. spectroscopic evidence for the formation of N- and O-bonded cyanato-derivatives of the hexachlorophosphate (PCl_6^-) ion, formed by different preparative routes.

The method of pairwise interactions, originally proposed by Vladimiroff and Malinowski for tetrahedral species,[11] but since applied to octahedral complexes of niobium,[12] antimony[13] and tin[14,15] as well as phosphorus,[6–10,16] has been used to assign isomeric configurations. It is particularly valuable where chemical reasons preclude the isolation of individual compounds, as in the azidochlorophosphates(V) or chlorothiocyanatophosphates(V), where only the fully-substituted ions $[P(N_3)_6]^-$ (Ref. 5) or $[P(NCS)_6]^-$ (Ref. 8) have been isolated as salts with suitable large cations. A preliminary account of this work has been presented at the International Conference on Phosphorus Chemistry, held in Nice in September 1983.[17]

RESULTS AND DISCUSSION

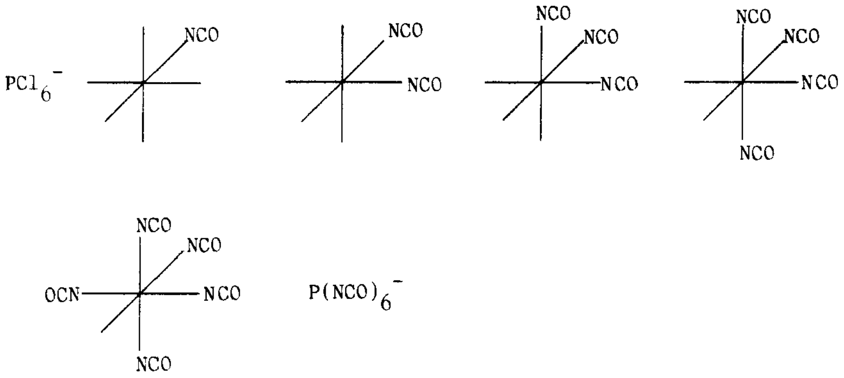
(1) N-bonded cyanato-complexes

The reaction of phosphorus(V) chloride with LiNCO in CH_2Cl_2 solution led to the gradual formation (within 1d) of an intense ^{31}P n.m.r. signal at 16.2 ppm, possibly due to a molecular chlorocyanatophosphorus(V) compound,[21] together with smaller resonances at 38.7 (unassigned), 3.3 ($POCl_3$) and -12.9 ($POCl_2(NCO)$[1]) ppm. Addition of $(n\text{-}C_5H_{11})_4NCl$ to this solution yielded a series of peaks between -270 and -390 ppm, as shown in Table I, with a corresponding reduction in intensity of the signal at 16.2 ppm. These signals may reasonably be ascribed to complexes involving six-coordinate phosphorus, and from the large high field shifts compared with those of the species described in the following section they are deduced to arise from N- rather than O-bonded isomers. Shifts for six-coordinate phosphorus complexes with ligands bonding through nitrogen such as NCS^- [8] or N_3^- [6,7] are usually to higher field of those with oxygen donor ligands, as exemplified in section (2). Addition of more chloride caused a simplification of the spectrum in this region, with just two resonances visible at -280.4 and -298.2 ppm, the latter readily assigned to the PCl_6^- ion.[22] After one day, only the PCl_6^- signal remained in this area, and the concentrations of $POCl_3$ and $POCl_2(NCO)$ had increased. The peak at -280.4 ppm is ascribed to $[PCl_5(NCO)]^-$, since it was the last of the six-coordinate phosphorus species other than PCl_6^- to be present. Assignment of the highest field resonance ($\delta - 388.4$ ppm) to $[P(NCO)_6]^-$ enabled the pairwise parameters[11-16] to be evaluated. The chemical shifts calculated on this basis were refined by a least squares fit of the observed data, and are given in Table I. The final pairwise terms used were Cl : Cl -24.76, Cl : NCO -20.28 and NCO : NCO -32.47 ppm. Only one of the possible isomers for $n = 2$, 3 or 4 was detected in each case, and, although perfect agreement is not obtained, these may be assigned on the basis of the calculated values as the cis-, fac- and cis-isomers respectively. The pattern of

TABLE I

Calculated and observed shifts for $PCl_{6-n}(NCO)_n^-$ anions in CH_2Cl_2 ppm.

Ion	δ ^{31}P (ppm) Calculated	δ ^{31}P (ppm) Observed
PCl_6^-	-297.1	-298.2
$PCl_5(NCO)^-$	-279.2	-280.4
cis-$PCl_4(NCO)_2^-$	-278.0	
		-274.0
trans-$PCl_4(NCO)_2^-$	-261.2	
fac-$PCl_3(NCO)_3^-$	-293.4	
		-290.0
mer-$PCl_3(NCO)_3^-$	-276.7	
cis-$PCl_2(NCO)_4^-$	-308.8	
		-315.9
trans-$PCl_2(NCO)_4^-$	-292.1	
$PCl(NCO)_5^-$	-340.9	-340.0
$P(NCO)_6^-$	-389.6	-388.4



SCHEME 1 Pattern of substitution in $PCl_{6-n}(NCO)_n^-$.

substitution parallels that in the azidochlorophosphates(V),[6,7] as shown in Scheme 1. N-bonded cyanate, like azide, thus seems to exert a directing influence on subsequent substitution, favouring the cis position. The presence of small amounts of the other isomers might possibly not have been detected, but all the major peaks in this region of the spectrum may be assigned as shown. The pairwise treatment accounts satisfactorily for the initial downfield shift caused by replacement of Cl by NCO, followed by an upfield shift as the number of NCO groups present increases beyond two, lending some support to its use for this system.

(2) O-bonded cyanato-complexes

Since PCl_6^- undergoes ligand exchange with $P(NCS)_3$ to give chlorothiocyanatophosphates in which phosphorus is six-coordinate,[8] the analogous reaction of PCl_6^- with $P(NCO)_3$ was attempted in $MeNO_2$ solution. Rapid exchange to produce PCl_3 and $PCl_2(NCO)$ was observed, as well as formation of small quantities of $POCl_3$ and $POCl_2(NCO)$, and weak transient signals at -282.0 $[PCl_5(NCO)]^-$ and -203.6 ppm. Similarly, in MeCN as solvent this reaction yielded resonances due to $PCl_{3-n}(NCO)_n$ $(0 \leqslant n \leqslant 3)$ and $POCl_{3-n}(NCO)_n$ $(0 \leqslant n \leqslant 2)$, together with new signals at -197.4 and -162.0 ppm. These high field peaks appear to arise from species in which phosphorus is six-coordinate, clearly different from those ascribed to N-bonded cyanato-complexes, and are assigned to O-bonded isomers on the basis of their lower field chemical shifts, by comparison with the values for known six-coordinate anions containing P—O bonds (e.g. the anion $[(C_6H_4O_2)PCl_4]^-$ has δ ^{31}P -157.3 ppm in CH_2Cl_2 solution).[23]

Although ligand exchange was fast, insufficient $P(NCO)_3$ solution could be added to effect complete exchange and simultaneously keep the high field signals readily detectable. This problem was overcome by reacting PCl_3 with NaNCO in MeCN as solvent in the presence of $(n\text{-}C_5H_{11})_4N^+PCl_6^-$. PCl_3 and NaNCO yield the compounds $PCl_{3-n}(NCO)_n$ $(0 \leqslant n \leqslant 3)$, which then exchange with PCl_6^-, giving $[PCl_{6-n}(OCN)_n]^-$ and more PCl_3, thus restarting the cycle. Several new resonances were now found between -150 and -220 ppm, as shown in Table II; the strongest peaks in the spectrum were due to $POCl_2(NCO)$ at -9.8 and $POCl(NCO)_2$ at

TABLE II

Calculated and observed shifts for $PCl_{6-n}(OCN)_n^-$ anions in CH_3CN (ppm)

Ion	δ ^{31}P (ppm)	
	Calculated	Observed
PCl_6^-	−296.5	−298.2
$PCl_5(OCN)^-$	−252.0	—
cis-$PCl_4(OCN)_2^-$	−217.8	−214.4
trans-$PCl_4(OCN)_2^-$	−207.4	−203.6, −204.7[a]
fac-$PCl_3(OCN)_3^-$	−193.9	−197.4, −195.1[a]
mer-$PCl_3(OCN)_3^-$	−183.5	
cis-$PCl_2(OCN)_4^-$	−170.0	−172.5
trans-$PCl_2(OCN)_4^-$	−159.6	−162.0
$PCl(OCN)_5^-$	−156.4	−156.4
$P(OCN)_6^-$	−153.1	−150.9

[a] From the $(n\text{-}C_5H_{11})_4NPCl_6$–$(n\text{-}C_5H_{11})_4NCl$–AgNCO system in CH_2Cl_2.

−27.5 ppm,[1] and smaller signals were apparent at 98.4 ($P(NCO)_3$[1]), 111.3, 79.1 and −32.4 ppm, the latter not readily assignable to known cyanato-derivatives of phosphorus.

The peaks in the six-coordinate region were assigned via the method of pairwise interactions, on the assumption that the two resonances at lowest field (−156.4 and −150.9 ppm) arise from $[PCl(OCN)_5]^-$ and $[P(OCN)_6]^-$, respectively. The least squares best fit values are given in Table II, calculated from Cl : Cl −24.71, Cl : OCN −13.58 and OCN : OCN −12.76 ppm. In this system both isomers of $[PCl_4(OCN)_2]^-$ and $[PCl_2(OCN)_4]^-$ were found (the number of signals observed shows that there is not a marked stability associated with a particular configuration for $n = 2$, 3 or 4, unlike N-bonded species), but no signals assignable to $[PCl_5(OCN)]^-$ or mer-$[PCl_3(OCN)_3]^-$ were detected. These results suggest that $[PCl_5(OCN)]^-$ may be unstable to ligand redistribution, since it would have been expected to be present at higher chloride concentrations, if stable. Similar instability of the first member of a substitution series has been observed in some six-coordinate fluorophosphate derivatives.[4] None of these anions was stable in solution, decomposition to phosphoryl species being complete within one day.

Attempted direct substitution by AgNCO into $(n\text{-}C_5H_{11})_4NPCl_6$ in CH_2Cl_2 solution led only to the slow formation of $POCl_3$ and $POCl_2(NCO)$. LiNCO caused a similar, but even slower, reaction. The experiment with AgNCO was repeated in the presence of excess $(n\text{-}C_5H_{11})_4NCl$ to suppress any dissociation of the hexachlorophosphate ion to molecular species, which could provide a route to decomposition. A mildly exothermic reaction occurred, and ^{31}P n.m.r. signals were observed from $POCl_3$, $POCl_2(NCO)$ and $POCl(NCO)_2$ as well as from PCl_6^-, together with new resonances at −204.7 and −195.1 ppm, assigned to trans-$[PCl_4(OCN)_2]^-$ and fac-$[PCl_3(OCN)_3]^-$ as shown in Table II. Species with more OCN groups attached to phosphorus were not detected, probably because of the presence of excess chloride ions.

The results thus show that linkage isomers of the cyanate ligand attached to six-coordinate phosphorus may be prepared in solution and identified spectroscopically, although their instability has so far precluded the isolation of individual members of either series. The method of pairwise interactions has proved very useful for assigning probable isomeric configurations to the complexes.

EXPERIMENTAL

All manipulations, including n.m.r. sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo. Chemicals of the best available commercial grade were used, in general without further purification, except for tetraalkylammonium chlorides, which were dried as described previously.[8] Anhydrous LiNCO was prepared by a method similar to that used for LiN_3;[18] a 1 : 2 molar ratio of $Li_2SO_4 \cdot H_2O$ and KNCO was dissolved in the minimum quantity of water with stirring and heating. A large volume of EtOH was added, and the resultant precipitate filtered off. The solution was evaporated and the crude product was dried at 303 K. Elemental analysis showed the absence of potassium. The solid was digested for 5 minutes with EtOH, the solution was filtered and evaporated to give a white solid, an aqueous solution of which did not give a precipitate with $BaCl_2$ solution (Found, C, 24.4; N, 30.8; Li, 13.5%; LiNCO requires C, 24.5; N, 28.6; Li, 14.2%). The compound $(n\text{-}C_5H_{11})_4N^+PCl_6^-$ was prepared as described previously.[7] For reactions involving $P(NCO)_3$ and requiring a polar organic solvent such as MeCN or $MeNO_2$, a solution of PCl_3 in that solvent was treated with excess NaNCO.[19] The solution was filtered and used as such. Stock solutions of $P(NCO)_3$ were stored at 243 K to reduce polymer formation.

^{31}P n.m.r. spectra were recorded at 307.2 K on the Fourier transform spectrometer, as indicated previously.[8] Chemical shifts were measured relative to external H_3PO_4, with the downfield direction taken as positive. Microanalyses for C, H, N, P and Cl were obtained as described in earlier papers,[7,8,20] and lithium analyses were obtained by atomic absorption spectroscopy.

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