

Structures of the Mixed Azidochlorophosphates $[\text{PCl}_{6-n}(\text{N}_3)_n]^-$

By KEITH B. DILLON,* ANDREW W. G. PLATT, and THOMAS C. WADDINGTON
(Chemistry Department, University of Durham, South Road, Durham DH1 3LE)

Summary The series of azidochlorophosphates $[\text{PCl}_{6-n}(\text{N}_3)_n]^-$ have been identified in solution by ^{31}P n.m.r. spectroscopy; the structure of the single isomer formed preferentially in each case when $n = 2, 3,$ or 4 has been deduced from pairwise interactions.

ALTHOUGH the hexa-azidophosphate ion is known^{1,2} (^{31}P n.m.r. δ 184.1 p.p.m. upfield from 85% $\text{H}_3\text{PO}_4^{\text{aq}}$), mixed azidochlorophosphates have not been reported. We have identified the complete series of ions, formed by careful stepwise addition of LiN_3 to a CH_2Cl_2 solution of $(n\text{-C}_5\text{H}_{11})_4\text{NPCl}_6$, by means of ^{31}P n.m.r. spectroscopy. Six new resonances downfield from the $[\text{PCl}_6]^-$ signal were detected, in addition to signals from decomposition products.³ From the changes in relative intensity with amount of added N_3^- , these are assigned as shown in Table 1. Isolation of the compounds, which would in any case

TABLE 1. $\delta^{31}\text{P}$ (p.p.m.) for $[\text{PCl}_{6-n}(\text{N}_3)_n]^-$ ions in CH_2Cl_2 solution.

n	0	1	2	3	4	5	6
$\delta^{31}\text{P}$	298.2	243.5	206.4	183.4	171.2	167.7	180.0

be extremely difficult because of the presence of other substitution and decomposition products, was not attempted in view of their probable dangerously explosive nature.^{1,2} The shift for $[\text{P}(\text{N}_3)_6]^-$ is in good agreement with the literature value from a different solvent.² There are two points of particular interest in the results. Firstly, the shift values go through a minimum at $[\text{PCl}(\text{N}_3)_5]^-$, with both $[\text{PCl}_2(\text{N}_3)_4]^-$ and $[\text{P}(\text{N}_3)_6]^-$ having signals at higher field. Secondly, one isomer appears to be formed preferentially for the ions where $n = 2, 3,$ or 4 , although two are possible in each case.

We have been able to assign structures to these species on the basis of pairwise interactions,⁴⁻⁶ where the chemical shift may be derived mathematically by summing interactions between adjacent ligands attached to the central atom, which act along the edges of the co-ordination polyhedron. There are twelve such interactions for an octahedron, of three possible types in this case, *i.e.*, Cl-Cl, Cl- N_3 and $\text{N}_3\text{-N}_3$. The Cl-Cl term is taken as 24.9 p.p.m. from the shift for $[\text{PCl}_6]^-$, and the Cl- N_3 term as 11.2 p.p.m. from the value for $[\text{PCl}_5\text{N}_3]^-$ (Table 1). The chemical shift of *trans*- $[\text{PCl}_4(\text{N}_3)_2]^-$ can then be evaluated as 189.2 p.p.m., since there are no $\text{N}_3\text{-N}_3$ interactions. This differs considerably from the experimental shift (206.4 p.p.m.), which is therefore assumed to be due to the *cis*-isomer. Hence the $\text{N}_3\text{-N}_3$ term is calculated as 14.7 p.p.m. The shifts for all subsequent substitutes including the

TABLE 2. $\delta^{31}\text{P}$ (p.p.m.) predicted from pairwise interactions for $[\text{PCl}_{6-n}(\text{N}_3)_n]^-$ ions

Ion	Calculated $\delta^{31}\text{P}$ /p.p.m.		Experimental $\delta^{31}\text{P}$ /p.p.m.
	A	B	
<i>cis</i> - $[\text{PCl}_4(\text{N}_3)_2]^-$		206.7	206.4
<i>trans</i> - $[\text{PCl}_4(\text{N}_3)_2]^-$	189.2	189.2	
<i>fac</i> - $[\text{PCl}_3(\text{N}_3)_3]^-$	186.0	186.9	183.4
<i>mer</i> - $[\text{PCl}_3(\text{N}_3)_3]^-$	168.8	169.4	
<i>cis</i> - $[\text{PCl}_2(\text{N}_3)_4]^-$	165.6	167.1	171.2
<i>trans</i> - $[\text{PCl}_2(\text{N}_3)_4]^-$	148.4	149.6	
$[\text{PCl}(\text{N}_3)_5]^-$	162.4	164.8	167.7
$[\text{P}(\text{N}_3)_6]^-$	176.4		180.0

fac- and *mer*-isomers of $[\text{PCl}_3(\text{N}_3)_3]^-$ and the *cis*- and *trans*-isomers of $[\text{PCl}_2(\text{N}_3)_4]^-$, can now be evaluated (Table 2, column A). Although perfect agreement with the experimental values is not obtained, we conclude that *fac*- $[\text{PCl}_3(\text{N}_3)_3]^-$ and *cis*- $[\text{PCl}_2(\text{N}_3)_4]^-$ are the preferred forms in solution, corresponding to an overall pattern of *cis* substitution by azido-groups. Support for the use of the pairwise interaction method is provided by the prediction of a minimum in the shift values at $[\text{PCl}(\text{N}_3)_5]^-$, as observed.

Alternatively, if the assignment of the signal at 180 p.p.m. to $[\text{P}(\text{N}_3)_6]^-$ is taken as correct, the $\text{N}_3\text{-N}_3$ term can be evaluated directly as 15.0 p.p.m. The shifts calculated for the ions where $n = 2, 3, 4,$ or 5 on this basis, but using the values given above for the Cl-Cl and Cl- N_3 terms, are shown in column B of Table 2. The shifts for species with $\text{N}_3\text{-N}_3$ interactions are all slightly higher as a result, without changing the deductions as to which isomers are present. Moreover the shift predicted for *cis*- $[\text{PCl}_4(\text{N}_3)_2]^-$ is in excellent agreement with the experimental value.

Pairwise interactions have been used previously to identify isomers in octahedral bromochloro-complexes of niobium⁵ and antimony,⁶ where the chemical shift differences between successive ions are much larger than in this instance, making differentiation easier. In both systems, similar conclusions were reached about the preferential formation of *cis*- rather than *trans*-isomers. The shift sequences followed a regular trend because of the magnitude of the pairwise interaction terms, however, and no minimum (or maximum) was apparent in the results. The successful prediction of a chemical shift minimum in the azidochlorophosphate series should lend some confidence to the application of the pairwise interaction method to a wide variety of inorganic complexes.

We thank the S.R.C. for the award of a maintenance grant (to A.W.G.P.).

(Received, 28th June 1979; Com. 687.)

¹ H. W. Roesky, *Angew. Chem. Internat. Edn.*, 1967, **6**, 637.

² P. Volgnandt and A. Schmidt, *Z. anorg. Chem.*, 1976, **425**, 189.

³ K. B. Dillon, A. W. G. Platt, and T. C. Waddington, *J.C.S. Dalton*, submitted for publication.

⁴ T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, 1967, **46**, 1830; J. S. Hartman and J. M. Miller, *Inorg. Chem.*, 1974, **13**, 1467; K. B. Dillon and J. M. Miller, unpublished work.

⁵ R. G. Kidd and H. G. Spinney, *Inorg. Chem.*, 1973, **12**, 1967.

⁶ R. G. Kidd and H. G. Spinney, paper presented at 5th Internat. Conf. on Non-aqueous Solutions, Leeds, 1976.