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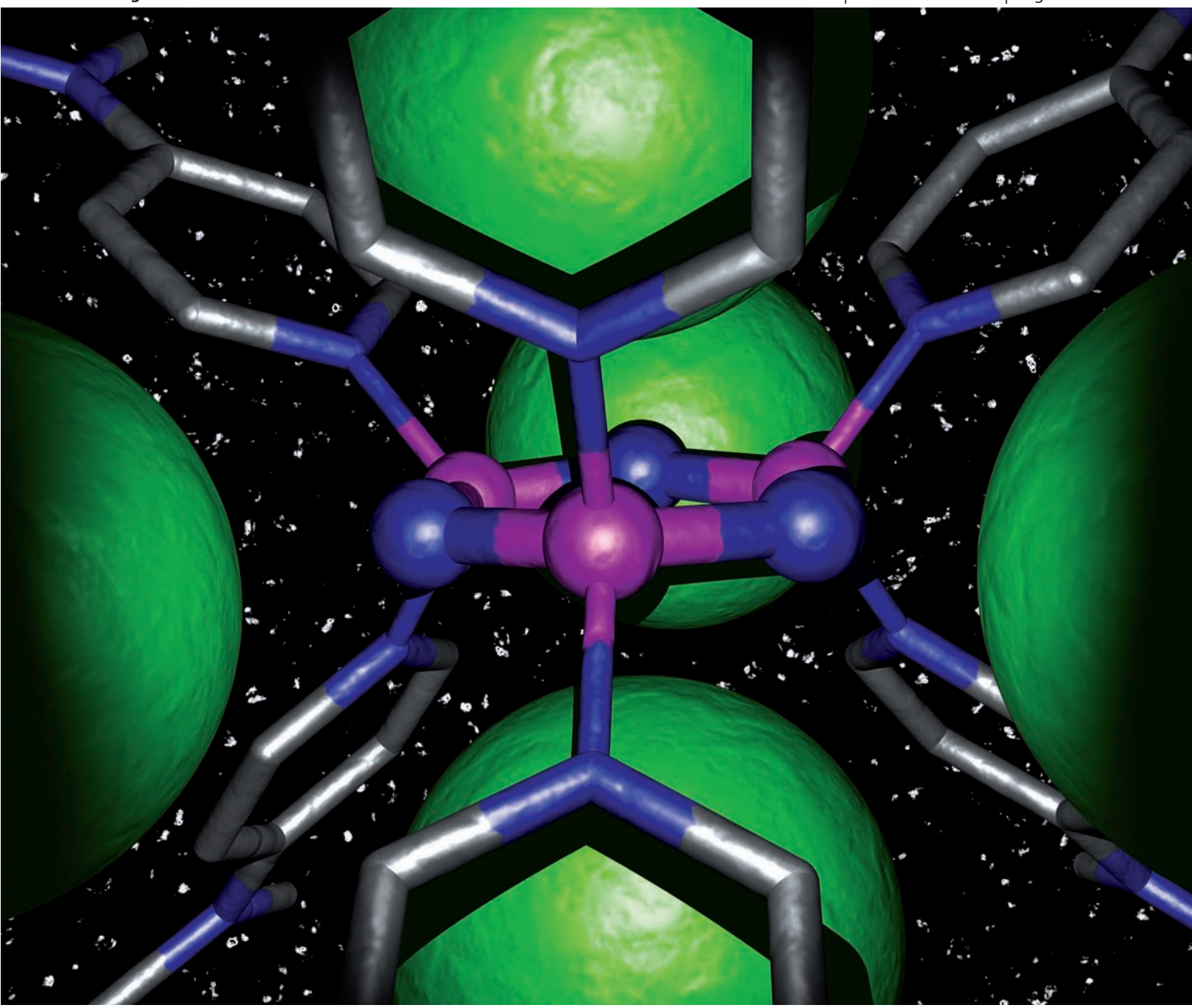

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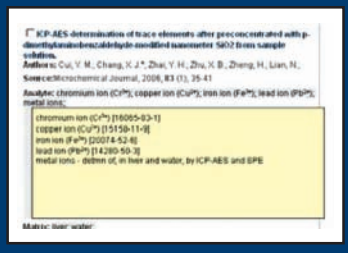

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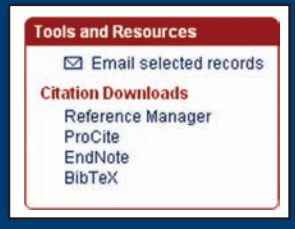


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# The N-donor stabilised cyclotriphosphazene hexacation $[P_3N_3(DMAP)_6]^{6+}$†

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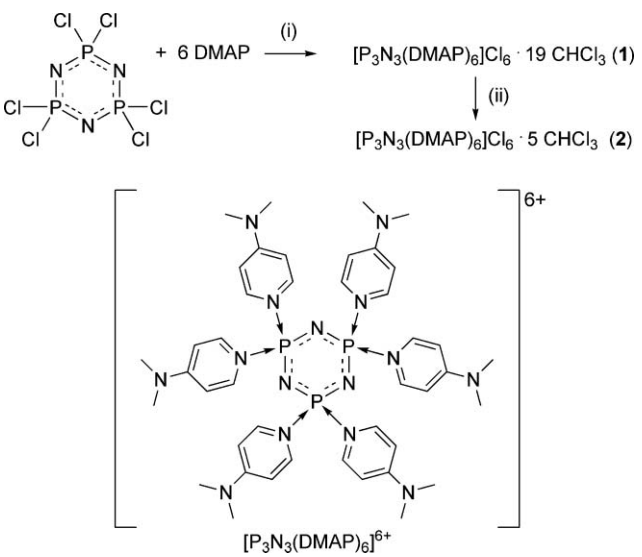
**The cyclotriphosphazene $P_3N_3Cl_6$ reacts with six equivalents of DMAP (4-(dimethylamino)pyridine) in superheated chloroform to form crystals of composition $[P_3N_3(DMAP)_6]Cl_6 \cdot 19CHCl_3$ comprising $[P_3N_3(DMAP)_6]^{6+}$ ions, which host five chloride ions in basket-type cavities on either side of the ring and at equatorial positions *via* tetradentate *ortho*-H-donor arrangements.**

Cyclic and polymeric phosphazenes are renowned for the extreme robustness of their phosphorus–nitrogen backbones, enabling substitution reactions of side groups with retention of the PN structure.[1,2] Cyclotriphosphazene cations have been proposed as intermediates in the ring opening polymerisation of $P_3N_3Cl_6$,[1] but they, as well as their adducts with neutral donor ligands, remained elusive and evaded structural characterisation. Nonetheless, neutral heterocyclic N-donors, L, have been shown to stabilise a variety of mononuclear P(V) species, including $L_2–PO_2^+$,[3,4] $L_2–PS_2^+$,[5] $L–PS_3^-$,[6] $L_2–P(NR)_2^+$ [7] and $L–Cl_2P{=}NSiMe_3^+$,[8] as well as the P(III) species $L_2–PO^+$,[4] $R_2P^+–L$, $RN{\equiv}P^+–L$ and $RN{\equiv}P^+–L_2$.[9] Considering the strength of the phosphazene ring structure, we were curious to know whether the ring segment $[P_3N_3]^{6+}$ could be stabilised exclusively with neutral donor molecules, and how the resulting hexacations were embedded within the supramolecular structure of the solid state.

An alleged synthesis of $[P_3N_3(DMAP)_6]Cl_6$ was reported by Vapirov *et al.* in 1986, which involved the combination of $P_3N_3Cl_6$ and six equivalents of DMAP in toluene.[10] We followed that procedure, only to obtain ill-defined product mixtures, as indicated by $^{31}P\{^1H\}$ MAS NMR. Evidently, premature precipitation of partially substituted $[P_3N_3Cl_{6-x}(DMAP)_x]Cl_x$ occurred under the reaction conditions described. We have now found that the reaction goes to completion if it is carried out in superheated chloroform at 100 °C for 20 min in a microwave reactor.‡ The crystalline product, **1**, consists of thin plates, which rapidly degrade in the absence of mother liquor due to the loss of solvent. The X-ray crystal structure§ shows an overall composition of $[P_3N_3(DMAP)_6]Cl_6 \cdot 19CHCl_3$ (Scheme 1).

In the crystal structure, the hexacation $[P_3N_3(DMAP)_6]^{6+}$ occupies a general position in the asymmetric unit and has approximately $D_{3h}$ symmetry. The hexacation furnishes basket type arrangements of three DMAP ligands on either side of the phosphazene ring (Fig. 1). The P–N bonds of the planar $P_3N_3$ ring measure, on average, 1.561 Å, which is at the short end of the spectrum of ring bond lengths in homoleptically-substituted cyclotriphosphazenes.[2] The average $P–N_{DMAP}$ bond length in **1** (1.706 Å) corresponds to that of $DMAP–P(Cl_2){=}NSiMe_3^+$ (1.713 Å)[8] and is somewhat longer than the exocyclic $P–N_{amino}$ bond in amino derivatives $(RNH)_6P_3N_3$ (1.66 Å).[11] The phosphazene ring in **1** describes a regular hexagon (N–P–N 120.8°, P–N–P 119.0°), while the exocyclic N–P–N angles toward the DMAP ligands measure 99.9°.

The hexacation provides suitable binding pockets for five chloride ions (Fig. 1), which are held in close proximity due to strong ion pairing interactions. Each basket, composed of three DMAP ligands, accommodates one chloride ion. The shortest contacts between the basket-contained chloride ions and the hexacation are towards the P-bonded nitrogen centres of the DMAP ligands, with an average N···Cl distance of 3.31 Å. In addition, the *ortho*-H atoms of the DMAP ligands offer three tetradentate binding sites for chloride ions at equatorial positions around the ring. This supramolecular arrangement has features similar to those of previous anion receptors, in which the anion is located above the nitrogen of a metal-coordinated pyridine, or held above an electron-deficient ring by C–H···Cl interactions.[12]




**Scheme 1** Synthesis of **1** and **2**. Reaction conditions: (i) $CHCl_3$/100 °C/microwave, (ii) 0.1 torr/r.t.

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† Electronic supplementary information (ESI) available: Solid state NMR spectra and thermogravimetric analysis of **2**. See DOI: 10.1039/b713847d

 

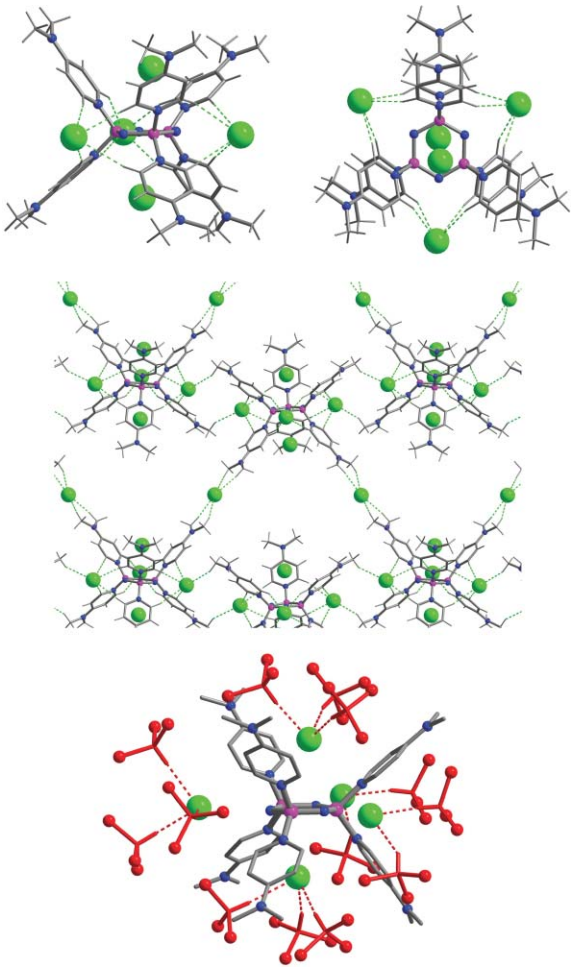

**Fig. 1** Crystal structure of **1**. Top: Host–guest assembly of the $[P_3N_3(DMAP)_6]^{6+}$ ion and five chloride ions. Middle: Extended structure of the $[P_3N_3(DMAP)_6]Cl_6$ unit (chloroform molecules have been omitted). Bottom: Coordination sphere of chloroform around the $\{[P_3N_3(DMAP)_6]Cl_5\}^+$ assembly; $Cl^-$ ions, green; P, purple; N, blue; chloroform, red.

The sixth chloride ion in **1** interacts with the methyl groups of two DMAP ligands, resulting in a networked structure.

The solvent accessible volume of **1** amounts to 71%. It is occupied by nineteen molecules of chloroform per $[P_3N_3(DMAP)_6]Cl_6$ unit, seventeen of which are engaged in coordinating the six chloride ions. Fig. 1 shows that the $\{[P_3N_3(DMAP)_6]Cl_5\}^+$ assembly is effectively complexed by thirteen chloroform molecules. The sixth, bridging, chloride ion is coordinated by four chloroform molecules. Some chloroform molecules are affected by disorder. However, we were able to resolve the disorder and obtain a suitable model with rational $Cl_3CH\cdots Cl^-$ contacts.[13] In addition, there are two lattice bound chloroform molecules per formula unit that are not coordinated to chloride ions.

Filtration and vacuum treatment of **1** produces colourless powder **2**, which melts under decomposition at 200 °C.‡ It dissolves in 1,1,2,2-tetrachloroethane, exhibiting a single resonance at $\delta$ 10.3 in its $^{31}P$ NMR spectrum. The $^1H$ NMR spectrum of the solution shows around five equivalents of chloroform per formula unit, which gives an overall composition of $[P_3N_3(DMAP)_6]Cl_6{\cdot}5CHCl_3$. The $^{31}P\{^1H\}$ MAS NMR spectrum of the solid consists of a sharp signal at $\delta$ 6.7, while the $^1H$–$^{13}C$ CP/MAS NMR spectrum verifies the presence of chloroform and mirrors the $^{13}C$ resonances of the DMAP ligands observed in solution.

**Table 1** B3LYP/6-31G* NPA charges at experimental geometries

| L in $P_3N_3L_6$ | P | N | Ring |
|---|---|---|---|
| F | 2.57 | −1.49 | 3.24 |
| DMAP[a] | 2.46 | −1.45 | 3.02 |
| $NH_2$ | 2.30 | −1.53 | 2.31 |
| Cl | 1.88 | −1.45 | 1.29 |

[a] As part of the $\{[P_3N_3(DMAP)_6]Cl_5\}^+$ assembly in **1**.

The thermogravimetric analysis of **2** correlates well with the loss of five chloroform and six DMAP molecules from $[P_3N_3(DMAP)_6]Cl_6{\cdot}5CHCl_3$ when heated above 260 °C, leaving a residual weight that corresponds to $PNCl_2$. Below 260 °C, the TGA trace displays a gradual weight loss lacking distinct steps, suggesting the absence of a pure desolvated compound $[P_3N_3(DMAP)_6]Cl_6$ at any given temperature during the heating process. The weight loss accelerates at around 200 °C, at which point the sample weight corresponds to $[P_3N_3(DMAP)_6]Cl_6{\cdot}CHCl_3$.

The formation of $[P_3N_3(DMAP)_6]Cl_6$ from $P_3N_3Cl_6$ and DMAP appears to be reversible. Heating a solution of **2** in 1,1,2,2-tetrachloroethane regenerates $P_3N_3Cl_6$, accompanied by the formation of trichloroethylene and the elimination of DMAP·HCl. The $^{31}P$ NMR spectrum of the heated mixture consisted of a sole signal at $\delta$ 21.3, indicating a quantitative reaction, while $^1H$ NMR confirmed the emergence of trichloroethylene ($\delta$ 6.4).

Table 1 compares the B3LYP/6-31G* Natural Population Analysis (NPA) charges of $[P_3N_3(DMAP)_6]^{6+}$ with that of other cyclotriphosphazenes. It shows that the charge on phosphorus correlates with the electronegativity of the ligand, while the charge on nitrogen remains constant. The computations gave an overall charge of 3.02 for the $P_3N_3$ ring of the hexacation as part of the $[P_3N_3(DMAP)_6]Cl_5^+$ assembly, which implies that the positive charge of the hexacation is equally shared between the phosphazene ring and the DMAP ligands. The electrostatic potential map (Fig. 2) illustrates the extent to which the positive charge is distributed onto the DMAP ligands. In particular, the *ortho*-H positions that interact with the equatorially-arranged chloride ions exhibit a pronounced positive character.

In summary, we have shown that $P_3N_3Cl_6$ readily reacts with DMAP under appropriate reaction conditions to form

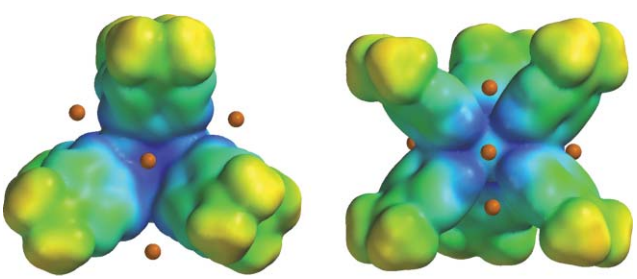

**Fig. 2** Electrostatic potential map of the $\{[P_3N_3(DMAP)_6]^{6+}$ ion in the presence of the five hosted chloride ions (positive regions are shown in blue).

$[P_3N_3(DMAP)_6]^{6+}$ ions. There is, to our knowledge, no structurally characterised example in p-block chemistry of such a highly charged ring system that is stabilised exclusively by neutral donor molecules. The reversibility of this reaction promises interesting applications for $[P_3N_3(DMAP)_6]^{6+}$ and related ions as intermediates in the synthesis of cyclo- and polyphosphazene derivatives. Moreover, the host's unique qualities toward chloride ions, the ability to accommodate a large amount of solvent in the crystal lattice and the suitability of solvothermal reaction conditions could pave the way for new main group-based framework materials.

We greatly acknowledge the EPSRC for financial support (grant no. GR/T07305/01) and thank Dr Hongjun Niu for the running of the TGA.

## Notes and references

‡ Synthesis of **1**: 60 mg of $P_3N_3Cl_6$ (0.173 mmol), 126 mg of DMAP (1.03 mmol) and 3 ml of chloroform were placed in a 10 ml CEM microwave reaction tube. The tube was then placed in the autosampler of a CEM Explorer™ microwave reactor and heated to 100 °C at 300 W power with cooling (Max Power™), using compressed air to maximise the energy input into the sample. The reaction was continued for 20 min to produce a supersaturated brown solution, which, on cooling to room temperature, yielded colourless plate-like crystals.

Synthesis of **2**: Crystals of **1** were filtered from the mother liquor and washed several times with chloroform. Subsequent treatment in a vacuum at 0.1 torr yielded a white powdery solid. Yield 190 mg (65.6%), m.p. 200 °C (decomp.); $^1$H NMR (400 MHz, $C_2D_2Cl_4$, $SiMe_4$): $\delta$ = 3.24 (s, 36H, $CH_3$), 6.94 (d, 12H, $^3J_{HH}$ = 7.2 Hz, *meta*-H), 7.30 (s, 5H, $CHCl_3$) and 9.80 (m, 12H, *ortho*-H); $^{13}C\{^1H\}$ NMR (100 MHz, $C_2D_2Cl_4$, $SiMe_4$): $\delta$ = 41.6 ($CH_3$), 78.2 ($CHCl_3$), 107.0 (*meta*-C), 141.0 (*ortho*-C) and 157.9 (*para*-C); $^{31}P\{^1H\}$ NMR (162 MHz, $C_2D_2Cl_4$, $H_3PO_4$ 85%): $\delta$ = 10.3. IR (Nujol): $\nu$(/cm$^{-1}$) = 1637, 1578, 1319, 1269, 1214, 1172, 1058, 822 and 735. Elemental analysis (%) calc. for $P_3N_{15}C_{42}H_{60}Cl_6\cdot(CHCl_3)_5$: C, 33.65; H, 3.90; N, 12.52%. Found: C, 32.04; H, 3.93; N, 12.74%.

§ Crystal data for **1**: $C_{42}H_{60}N_{15}P_3Cl_6\cdot 19CHCl_3$, $M_r$ = 3348.65, $T$ = 110 K, $P2_1/n$, $a$ = 20.056(8), $b$ = 26.748(10), $c$ = 25.940(10) Å, $\beta$ = 92.836(6)°, $V$ = 13899(9) Å$^3$, $Z$ = 4, $R1$ ($I > 2\sigma(I)$) = 0.0958, w$R2$ (all data) = 0.2304.[14] Crystals of **1** diffracted to only low resolution due to the large amount of more or less diffuse chloroform in the unit cell, thus the data were truncated at 1.1 Å. P and non-disordered Cl atoms were refined anisotropically. C and N atoms were refined isotropically to maintain a sufficient data/parameter ratio. Seven of the nineteen chloroform molecules are disordered. Their atom positions were split over two positions and refined using similar distance and similar $U$ restraints. H-atoms were fixed in calculated positions at their parent C atoms. CCDC 655911. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713847d

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