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Synthesis, X-ray structure and coordination to $Mn(CO)_3(bipy)^+$ of the cyclotriphosphazenes $N_3P_3(OC_5H_4N\text{-}2)_6$ and $N_3P_3(OC_5H_4N\text{-}4)_6$

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Abstract

The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ reacts with 2-hydroxypyridine ($HOC_5H_4N\text{-}2$) and 4-hydroxypyridine ($HOC_5H_4N\text{-}4$) in acetone in the presence of K_2CO_3, to give the hexasubstituted products $N_3P_3(OC_5H_4N\text{-}2)_6$ (**1**) and $N_3P_3(OC_5H_4N\text{-}4)_6$ (**2**). The structure of both compounds has been determined by X-ray diffraction. The hexafunctionalized cyclotriphosphazene $N_3P_3(OC_5H_4N\text{-}4)_6$ (**2**) is a better ligand than **1** and reacts with *fac*-$[Mn(OClO_3)(CO)_3(bipy)]$ in CH_2Cl_2 to give the hexacationic complex $[N_3P_3\{(OC_5H_4N)Mn(CO)_3(bipy)\}_6](ClO_4)_6$ (**3**).

Keywords: Phosphazene; Pyridine; Manganese; Carbonyl; Hexacations

1. Introduction

The synthesis of cyclophosphazenes bearing potential coordinating groups, and their complexes with the transition metals are of interest because they are useful models for high molecular weight polymers carrying different types of transition metal carbonyl and organometallic fragments [1]. In particular, the use of pendant pyridine ligands is of current interest [2] because they can be used to immobilize organometallic fragments [3] and to make Langmuir–Blodget films [4]. Here we describe the preparation, X-ray structures and ligand properties of the hexapyridine phosphazene derivatives $N_3P_3(OC_5H_4N\text{-}2)_6$ and $N_3P_3(OC_5\text{-}H_4N\text{-}4)_6$.

2. Results and discussion

Using a method described elsewhere [5], the hexachlorocyclotriphosphazene $N_3P_3Cl_6$ was allowed to react with 2-hydroxypyridine ($HOC_5H_4N\text{-}2$) in refluxing acetone in the presence of K_2CO_3, to give the hexasubstituted product $N_3P_3(OC_5H_4N\text{-}2)_6$ (**1**) (Fig. 1), as a white crystalline solid. The hydrochloride derivative has already been reported in a patent [6]. Similarly, the reaction with 4-hydroxypyridine ($HOC_5H_4N\text{-}4$) gave the analogue $N_3P_3(OC_5H_4N\text{-}4)_6$ (**2**), although with a much lower yield after a more laborious work-up (see Section 3). Because the isolation of the product required the addition of an ammonium salt, this may be due to the deprotonation of some of the 4-hydroxypyridine groups. However, decomposition in the reaction of halogenated phosphazenes with pyridine derivatives are not uncommon [2].

The spectroscopic data for the compounds are in accord with the formulation given in Fig. 1. Only selected IR data, e.g. ν(PN), ν(POC), and ν(ClO) are included, in Section 3.

Significant differences were observed between the mass spectra of the two compounds. In both cases the peaks corresponding to the parent molecule M overlap with those of the M-1 peaks. For **1** the signals of M were much weaker than for **2**, and there was also proportionately less M-1. In both spectra the expected peaks corresponding to the loss of one, two and three OC_5H_4N groups were observed, but there were also peaks corresponding to the loss of C_5H_4N fragments. Therefore the main fragmentation occurs at the P–O bonds and is more favourable for **1**. Rather unexpectedly, in the spectrum of **2** there was an intense peak at

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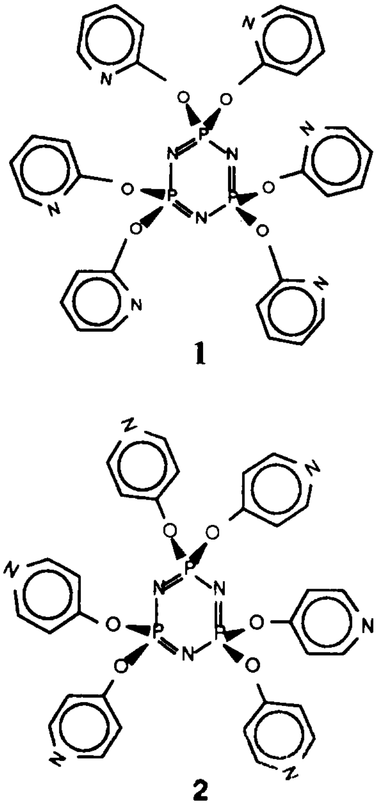


Fig. 1. Structural formulae of **1** and **2**.

172, corresponding to anion NH_4C_5–O–C_5H_4N which was absent in the case of **1**.

The structures of the two compounds were confirmed by X-ray diffraction. The results are summarized in Tables 1–5. The molecular structures with the atomic numbering are presented in Figs. 2 and 3.

In both molecules the N_3P_3 ring is slightly puckered. The largest deviation from the principal plane in **1** is that of atom N(3)(− 0.083(0.003) Å), and in **2** is that of N(1)(− 0.088(0.003) Å). The P–N distances, and the P–N–P and N–P–N angles are very close to those usually encountered in cyclic phosphazenes [7].

Each phosphorus atom bears two OC_5H_4N groups. Although the positions of the N atom are different in the two molecules, the dimensions of all the C_5H_4N rings are the same. The P–O distances (about 1.58 Å), the O–P–O angle (about 98°) and the P–O–C angles (121–129°) are typical of cyclic aryloxyphosphazenes [7]. The last angles, which are analogous to the important P–N–C angles in the aminophosphazenes [7], are far from the tetrahedral (sp3) values around the O atom, suggesting that there is some π electron delocalization between the pyridine ring and the phosphazene P atom.

In **1**, four of the six C_5H_4N ring planes (those of O(1), O(2), O(3) and O(6)) are roughly perpendicular to the N_3P_3 phosphazene ring, while the other two (those of O(4) and O(5)) form angles of about 24.66(8) and 39.0(2)° with it.

As a result of the relative disposition of all the aryloxy rings, there is no intramolecular stacking of the aromatic rings, and no intramolecular hydrogen-bonding interactions. However, the packing of the molecules within the crystal implies two weak intermolecular H bonds [8]: C(36)–H(36)–N(62) (H–N, 2.390(6) Å; C–H–N, 137.9(4)°, and C(54)–H(54)–O(4) (H–O, 2.462(7) Å; C–H–O, 151.7(6)°). Hydrogen-bonding in-

Table 1
Fractional positional and thermal parameters, with estimated standard deviations in parentheses for **1**

Atom	x	y	z	U_{eq} ($\times 10^2$ Å^2)
P(1)	−0.10362(3)	−0.12925(8)	−0.57215	3.49(3)
P(2)	−0.10789(3)	−0.31671(9)	−0.7310(1)	3.99(3)
P(3)	−0.18148(3)	−0.11215(8)	−0.7235(1)	3.77(3)
O(1)	−0.11746(9)	−0.1781(2)	−0.4567(2)	4.66(8)
O(2)	−0.05808(9)	−0.0244(2)	−0.5429(2)	4.58(8)
O(3)	−0.11821(9)	−0.4762(2)	−0.7147(2)	5.02(8)
O(4)	−0.06939(9)	−0.3265(2)	−0.8286(2)	4.84(9)
O(5)	−0.24129(8)	−0.1467(2)	−0.6971(2)	5.02(9)
O(6)	−0.19124(9)	0.0028(2)	−0.8091(2)	4.93(8)
N(1)	−0.0799(1)	−0.2570(3)	−0.6309(2)	3.95(9)
N(2)	−0.1579(1)	−0.2429(3)	−0.7767(2)	4.39(9)
N(3)	−0.1513(1)	−0.0517(3)	−0.6251(2)	3.70(9)
C(11)	−0.1491(1)	−0.1084(4)	−0.3852(3)	4.5(1)
N(12)	−0.1440(1)	0.0253(4)	−0.3766(3)	7.3(1)
C(13)	−0.1759(2)	0.0875(5)	−0.3053(4)	7.8(2)
C(14)	−0.2102(2)	0.0225(6)	−0.2463(4)	8.8(2)
C(15)	−0.2134(2)	−0.1156(7)	−0.2562(5)	11.5(3)
C(16)	−0.1819(2)	−0.1845(4)	−0.3281(4)	7.2(2)
C(21)	−0.0314(1)	0.0565(4)	−0.6150(3)	4.6(1)
N(22)	−0.0199(1)	0.0035(3)	−0.7050(3)	6.5(1)
C(23)	0.0093(2)	0.0818(5)	−0.7690(4)	8.6(2)
C(24)	0.0259(2)	0.2091(5)	−0.7449(5)	8.8(2)
C(25)	0.0121(2)	0.2613(5)	−0.6513(6)	10.4(2)
C(26)	−0.0176(2)	0.1827(4)	−0.5813(4)	7.4(2)
C(31)	−0.1501(1)	−0.5267(4)	−0.6351(3)	4.5(1)
N(32)	−0.1779(1)	−0.4389(3)	−0.5787(3)	4.9(1)
C(33)	−0.2092(2)	−0.4926(4)	−0.5039(4)	5.5(2)
C(34)	−0.2135(2)	−0.6287(5)	−0.4846(4)	6.4(2)
C(35)	−0.1846(2)	−0.7168(4)	−0.5465(4)	7.1(2)
C(36)	−0.1516(1)	−0.6666(4)	−0.6239(3)	5.5(1)
C(41)	−0.0181(1)	−0.3797(4)	−0.8339(3)	4.6(1)
N(42)	−0.0120(1)	−0.4646(3)	−0.9120(3)	6.2(1)
C(43)	0.0380(2)	−0.5104(5)	−0.9271(4)	8.0(2)
C(44)	0.0793(2)	−0.4726(6)	−0.8648(6)	9.5(2)
C(45)	0.0712(2)	−0.3835(6)	−0.7861(6)	11.2(3)
C(46)	0.0206(2)	−0.3324(5)	−0.7696(4)	7.7(2)
C(51)	−0.2746(1)	−0.0660(4)	−0.6368(3)	4.3(1)
N(52)	−0.3050(2)	0.0157(5)	−0.6859(3)	11.1(2)
C(53)	−0.3398(3)	0.0856(7)	−0.6262(6)	13.0(3)
C(54)	−0.3436(3)	0.0779(7)	−0.5247(6)	10.2(3)
C(55)	−0.3098(3)	−0.008(1)	−0.4755(5)	15.3(4)
C(56)	−0.2747(2)	−0.0837(7)	−0.5334(4)	11.1(3)
C(61)	−0.1512(2)	0.0551(4)	−0.8742(3)	5.2(1)
N(62)	−0.1328(2)	0.1724(4)	−0.8462(3)	8.4(2)
C(63)	−0.0975(3)	0.2277(7)	−0.9132(6)	11.7(3)
C(64)	−0.0798(2)	0.1657(8)	−1.0008(6)	10.7(3)
C(65)	−0.1011(2)	0.0453(8)	−1.0283(5)	10.3(3)
C(66)	−0.1379(2)	−0.0162(5)	−0.9631(4)	7.7(2)

$U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j \hat{A}_i \hat{A}_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 2
Fractional positional and thermal parameters, with estimated standard deviations in parentheses for **2**

Atom	x	y	z	U_{eq} ($\times 10^2$ Å^2)
P(1)	0.00000	0.1546(1)	0.75000	3.03(4)
P(2)	−0.05839(6)	0.36975(8)	0.69334(4)	3.41(3)
O(1)	0.0589(2)	0.0578(2)	0.7101(1)	3.92(8)
O(4)	−0.0178(2)	0.4115(2)	0.6226(1)	4.40(8)
O(3)	−0.1621(2)	0.4229(2)	0.6867(1)	4.46(8)
N(1)	−0.0638(2)	0.2288(2)	0.6987(1)	3.45(9)
N(2)	0.00000	0.4385(4)	0.75000	4.0(1)
C(11)	0.1001(2)	0.0745(3)	0.6469(2)	3.5(1)
C(12)	0.1706(3)	0.1550(4)	0.6375(2)	5.1(1)
C(13)	0.2111(3)	0.1598(4)	0.5740(2)	6.0(2)
N(14)	0.1863(3)	0.0890(4)	0.5219(2)	6.0(1)
C(15)	0.1179(3)	0.0114(5)	0.5342(2)	6.3(2)
C(16)	0.0724(3)	0.0004(4)	0.5948(2)	5.2(2)
C(31)	−0.2301(2)	0.3983(3)	0.7354(2)	4.0(1)
C(32)	−0.2987(3)	0.3166(4)	0.7201(2)	5.3(2)
C(33)	−0.3662(3)	0.2959(5)	0.7689(3)	6.9(2)
N(34)	−0.3679(3)	0.3500(4)	0.8291(2)	7.4(2)
C(35)	−0.3006(4)	0.4292(5)	0.8413(2)	6.8(2)
C(36)	−0.2295(3)	0.4570(4)	0.7966(2)	5.1(1)
C(41)	−0.0478(3)	0.3753(3)	0.5579(2)	4.4(1)
C(42)	0.0212(3)	0.3436(4)	0.5135(2)	5.7(2)
C(43)	−0.0075(4)	0.3139(4)	0.4465(2)	6.9(2)
N(44)	−0.0959(3)	0.3162(4)	0.4250(2)	7.0(2)
C(45)	−0.1574(4)	0.3500(6)	0.4689(2)	8.3(2)
C(46)	−0.1396(3)	0.3781(5)	0.5365(2)	7.3(2)

$U_{eq} = (\frac{1}{3})\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for **1**

Bond lengths			
P(1)–O(1)	1.583(2)	P(1)–O(2)	1.587(2)
P(2)–O(3)	1.604(2)	P(2)–O(4)	1.577(2)
P(3)–O(5)	1.581(2)	P(3)–O(6)	1.589(2)
P(1)–N(1)	1.580(3)	N(1)–P(2)	1.568(3)
P(2)–N(2)	1.567(3)	N(2)–P(3)	1.570(3)
P(3)–N(3)	1.579(3)	N(3)–P(1)	1.574(3)
Bond angles			
O(1)–P(1)–O(2)	98.0(1)	O(3)–P(2)–O(4)	98.2(1)
O(5)–P(3)–O(6)	98.6(1)	P(1)–O(1)–C(11)	125.6(2)
P(1)–O(2)–C(21)	124.7(2)	P(2)–O(3)–C(31)	122.7(2)
P(2)–O(4)–C(41)	129.1(2)	P(3)–O(5)–C(51)	124.9(2)
P(3)–O(6)–C(61)	123.6(2)	P(1)–N(1)–P(2)	120.7(2)
N(1)–P(2)–N(2)	119.3(1)	P(2)–N(2)–P(3)	121.6(2)
N(3)–P(3)–N(2)	117.8(1)	P(3)–N(3)–P(1)	121.6(2)
N(3)–P(1)–N(1)	118.2(1)		

Table 4
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for **2**

Bond lengths			
P(1)–O(1)	1.580(2)	P(2)–O(3)	1.587(2)
P(2)–O(4)	1.580(2)	P(1)–N(1)	1.574(3)
N(1)–P(2)	1.577(3)	P(2)–N(2)	1.572(2)
Bond angles			
O(3)–P(2)–O(4)	99.7(1)	P(1)–O(1)–C(11)	125.7(2)
P(2)–O(3)–C(31)	121.3(2)	P(2)–O(4)–C(41)	127.3(2)
P(1)–N(1)–P(2)	122.6(2)	N(1)–P(2)–N(2)	117.7(2)

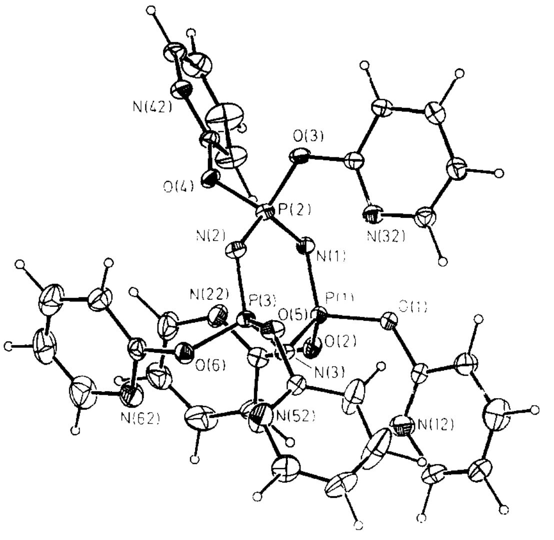


Fig. 2. A EUCLID drawing and numbering scheme for **1**.

teractions are important in the design of molecular solids involving substituted pyridones [9].

The relative orientations of the C_5H_4N rings are very different in **2** and **1**. In **2** there are three pairs of mutually parallel C_5H_4N rings (closely resembling the structure of $N_3P_3(OC_6H_4Cl\text{-}4)_6$ [10]) no intramolecular stacking and no significant intramolecular hydrogen-bonding interactions.

The hexafunctionalized phosphazene **1** gave no stable complexes with the cationic manganese carbonyl fragment $Mn(CO)_3(bipy)^+$, known to coordinate easily to pyridine [11]. The reaction of **1** with *fac*-[Mn($OClO_3$)$(CO)_3$(bipy)] resulted in a labile coordination of the phosphazene to $Mn(CO)_3(bipy)^+$, giving an unstable product. This was not surprising considering the severe steric hindrance around the donor *N* atoms of the pendant pyridine groups.

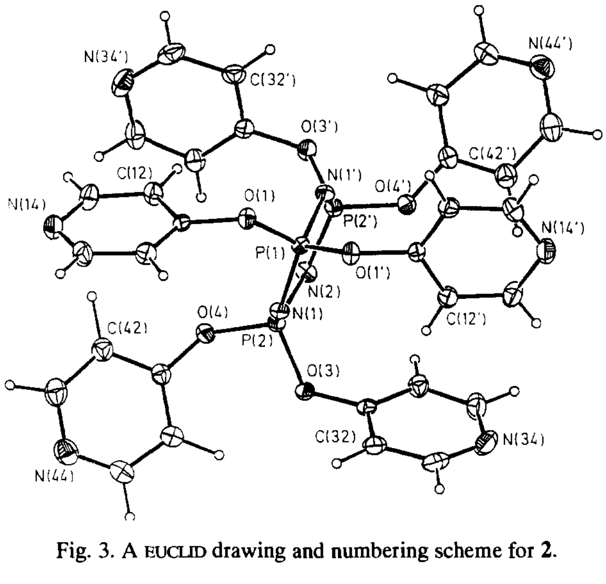


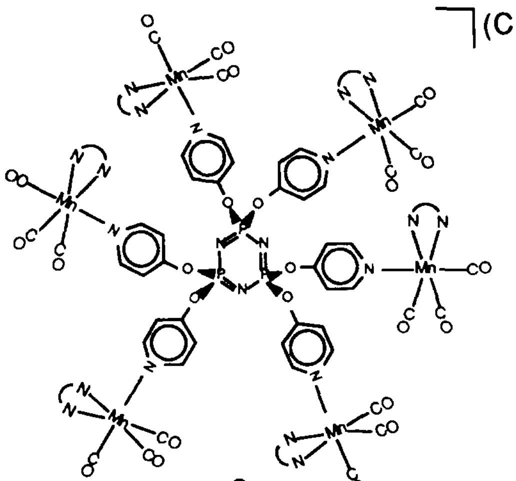
Fig. 3. A EUCLID drawing and numbering scheme for **2**.

However, the much less sterically encumbered **2** reacted rather quickly with an excess of *fac*-[Mn$(OClO_3)(CO)_3$(bipy)] in CH_2Cl_2, to form the stable hexacationic complex $[N_3P_3[(OC_5H_4N)Mn(CO)_3\text{-}(bipy)]_6]$ $(ClO_4)_6$ (**3**), which was isolated as a yellow solid. The analytical and spectroscopic data (experimental part) are in accord with the formulation shown in Fig. 4. The $^{31}P\{^1H\}$ NMR spectrum showed that the singlet corresponding to the three P atoms of the phosphazene ring was 3.4 ppm towards a lower frequency than in the free **2**. This is larger than the 1.7 ppm decrease observed on the formation of the related hexacationic manganese complexes with the hexanitrile ligand $N_3P_3(OC_5H_4CN\text{-}4)_6$ [12]. Clearly, this is due to the

Table 5
Crystal structure determination details for **1** and **2**

Crystallographic data		
Formula	$N_3P_3(OC_5H_4N\text{-}2)_6$	$N_3P_3(OC_5H_4N\text{-}4)_6$
Formula weight	699.50	699.50
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$C2/c$
Cell dimensions		
a (Å)	25.20(1)	14.158(7)
b (Å)	9.839(3)	11.152(2)
c (Å)	12.705(2)	19.603(5)
α (°)	90	90
β (°)	90	91.06(4)
γ (°)	90	90
Cell volume (Å^3)	3151.(2)	3095.(2)
Z	4	4
D_{calc} (g cm^{-3})	1.47	1.50
$F(000)$	1440	1440
Monochromated Mo Kα radiation		
λ (Å)	0.71073	
μ (cm^{-1})	2.41	2.45
Crystal size (mm)	0.40 × 0.26 × 0.23	0.26 × 0.16 × 0.10
Diffractometer	Enraf–Nonius CAD4	
Number of reflections for calculating unit cell; θ_{min} (°), θ_{max} (°)	25; 15, 20	25; 15, 20
Scan mode for data collection	ω–2θ	
Data reflection ranges	$-29 \leqslant h \leqslant 29$, $-11 \leqslant k \leqslant 11$, $-15 \leqslant l \leqslant 15$	$-14 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 23$
Number of total reflections measured	6314	3088
Number of unique reflections	5517	2731
R_{int}	0.025	0.030
Number of significant reflections, $I > 3\sigma(I)$	3921	1603
Number of drift correction, maximum, minimum	1.00, 0.99	1.05, 0.99
Absorption correction, maximum, minimum (DIFABS)	1.11, 0.88	1.15, 0.74
Structure solution and refinement		
Method for location of non-H atoms	Direct methods SHELXS-86	
Refinement method	Full-matrix least-squares non-H atom anisotropic SHELX-76	
Hydrogen atoms	Fixed calculated positions	
R	0.033	0.038
wR	0.033	0.040
S	1.7466	1.6260
g	0.0001	0.0006
Number of variables	433	266
Number of observed reflections	3921	1603
$(\Delta/\sigma)_{max}$	0.002	0.002
$(\Delta\rho)_{max}$ (electrons Å^{-3}), $(\Delta\rho)_{min}$ (electrons Å^{-3})	+0.32, −0.31	+0.38, −0.22

$\Sigma w(F_o - F_c)^2$ minimized, $w = 1/[\sigma^2(F_o) + gF_o^2]$ with $\sigma(F_o)$ from counting statistics.
The absolute structure of **1** was checked by the BIJVOET program resulting in $B = 0.49(3)$ for the 100 strongest Friedel pairs.



3

Fig. 4. Structural formula of **3**.

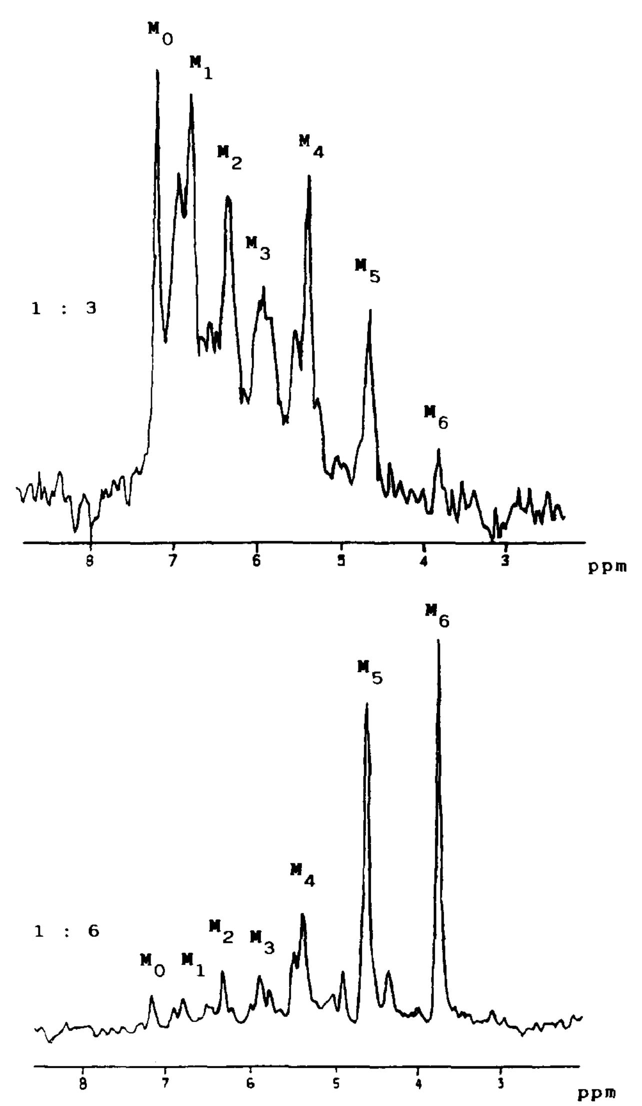


Fig. 5. ^{31}P NMR spectra corresponding to the final mixture from the reaction between **2** with three and six equivalents of $[Mn(O_3ClO)(CO)_3(bipy)]$. Mx represents $[N_3P_3(O\text{-}C_5H_4N\text{-}4)_{6-x}\{(OC_5H_4N)Mn(CO)_3(bipy)\}_x](ClO_4)_x$.

fewer bonds between the manganese fragment and the phosphazene ring phosphorus in the pyridine derivative. Following the reaction of **2** with different amounts of *fac*-$[Mn(O_3ClO)(CO)_3(bipy)]$ by ^{31}P $\{^1H\}$ NMR spectroscopy (Fig. 5) revealed the signals corresponding to all the intermediate polymetallic complexes $[N_3P_3(OC_5H_4N\text{-}4)_{6-x}\{(OC_5H_4N)Mn(CO)_3(bipy)\}_x]$ $(ClO_4)_x$ for $x = 1$ to 6. ($\delta(CH_2Cl_2) = 7.15$ ($x = 0$), 6.9 ($x = 1$), 6.3 ($x = 2$), 5.9 ($x = 3$), 5.4 ($x = 4$), 4.6 ($x = 5$) and 3.8 ($x = 6$) ppm). Because of partial overlapping, it was not possible to characterize all the AB_2 spin systems present in the mixture. The typical AB_2 was well observed (see Fig. 5) only in the case of the pentametal derivative.

As with the hexacationic complexes with pendant nitriles [12], the conductivity of **3** in acetone varied almost linearly with the square root of the concentration ($r = 0.98$), with $\Lambda_0 = 530$ Ω^{-1} cm^2 mol^{-1}, which is very large [13]. However, the variation with concentration is much larger than for the other hexacationic derivatives [12]. This is probably due to the partial dissociation of the pyridine–manganese bonds in acetone solution revealed by ^{31}P $\{^1H\}$ NMR spectroscopy.

3. Experimental section

All reactions were carried out under dry dinitrogen with standard Schlenk techniques. The IR spectra were recorded with a Perkin–Elmer FT 1720-X spectrometer. NMR spectra were recorded on a Bruker AC-200 or AC-300 instrument.

The K_2CO_3 was dried at 140°C before use. The acetone was pre-distilled from $KMnO_4$ and further distilled from anhydrous $CaSO_4$. The hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (Strem Chemicals) was crystallized from hot hexane and dried in vacuo. The complex *fac*-$[Mn(O_3ClO)(CO)_3(bipy)]$ [11] was prepared by the published procedure.

3.1. Preparation of $N_3P_3(OC_5H_4N\text{-}2)_6$

A mixture of $N_3P_3Cl_6$ (0.4 g, 1.15 mmol), HOC_5NH_4 (0.812 g, 8.3 mmol) and K_2CO_3 (1.6 g, 11.6 mmol) was heated under reflux in acetone (50 ml) for 48 h. The volatiles were evaporated in vacuo and the residue extracted with CH_2Cl_2 for 5 h. Evaporation of the solvent in vacuo gave spectroscopically and analytically pure **1a** as a white solid (yield, 0.49 g (60%)).

Anal. Found: C, 51.7; H, 3.3; N, 17.4. $C_{30}H_{24}N_9O_6P_3$ Calc.: C, 51.5; H, 3.4; N, 18.0%. Mass spectroscopy (MS)*m/z* 699.5 (calc. 699.5).

IR (Nujol mull): ν(NP) 1185 (vs, br), ν(POC) 954 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.14 (d,d $J_{HH} = 2$ and 5 Hz); 7.59 (d,d,d $J_{HH} = 2$, 7 and 8 Hz), 7.13 (d, $J_{HH} = 8$ Hz), 7.02 (d,d $J_{HH} = 5$ and 7 Hz) ppm. ^{31}P

NMR ($CDCl_3$): δ 6.83 ppm. ^{31}P NMR (acetone): δ 7.9 ppm. ^{13}C NMR ($CDCl_3$): δ 157.7, 147.6, 139.2, 120.3, 114.3 ppm.

3.2. Preparation of $N_3P_3(OC_5H_4N\text{-}4)_6$

A mixture of $N_3P_3Cl_6$ (0.4 g, 1.15 mmol), HOC_5H_4N (0.7 g, 7.01 mmol) and K_2CO_3 (2 g, 14.5 mmol) was heated under reflux in acetone (20 ml) for 5 h. The volatiles were evaporated in vacuo and the residue extracted with acetone (4 × 15 ml). The solution was stirred with solid NH_4Cl for 0.5 h and evaporated to dryness. The residue was extracted with toluene (4 × 20 ml) and the extract was evaporated in vacuo to give a slightly yellow solid that was recrystallized from CH_2Cl_2–petroleum ether (yield, 0.15 g (19%)). Colourless crystals for X-ray diffraction were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution.

Anal. Found: C, 52.0; H, 3.4; N, 18.2. $C_{30}H_{24}N_9O_6P_3$ Calc.: C, 51.5; H, 3.4; N, 18.0%, MS: m/z 699.5 (calc. 699.5).

IR (Nujol mull): ν(NP) 1181 (vs), ν(POC) 952 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.5 (d), 6.9 (d, $J_{HH} = 6$ Hz) ppm. ^{31}P NMR ($CDCl_3$): δ 7.15 ppm. ^{31}P NMR (acetone): δ 8.6 ppm. ^{13}C NMR ($CDCl_3$): δ 157.1 (d, $J_{PC} = 2$Hz), 152.6, 116.4 ppm.

3.3. Preparation of $[N_3P_3\{(OC_5H_4N)Mn(CO)_3(bipy)\}_6](ClO_4)_6$ (3)

A mixture of $N_3P_3(OC_5H_4N\text{-}4)_6$ (0.07 g, 0.10 mmol) and *fac*-$[Mn(OClO_3)(CO)_3(bipy)]$ (0.30 g, 0.75 mmol) in dichloromethane (15 ml) was stirred for 0.5 h at room temperature in the absence of light. The mixture was filtered and concentrated to about 5 ml. Addition of diethyl ether gave a yellow solid that was washed with diethyl ether. The resulting product was recrystallized from CH_2Cl_2–diethyl ether as a microcrystalline orange solid (**3**) (yield, 0.23 g (75%)).

Anal. Found C, 41.2; H, 2.7; N, 9.0. $C_{108}H_{72}Cl_6Mn_6N_{21}O_{48}P_3$: Calc.: C, 42.3; H, 2.4; N, 9.6%.

IR (CH_2Cl_2). ν(CO) 2043s, 1955s, 1945s cm^{-1}. IR (Nujol mull): ν(PN) 1186 (vs, br), ν(ClO) 1092 (vs, br, ClO_4^-), ν(POC) 949 (m) cm^{-1}. ^1H NMR (acetone-d_6): δ 9.5 (m, bipy); 8.55 (m, bipy), 8.43 (d, $J_{HH} = 7$ Hz, OC_5H_4N), 8.3 (m, bipy), 7.94 (m, bipy), 7.13 (d, $J = 7$ Hz, OC_5H_4N) ppm. ^{31}P NMR (Cl_2CH_2): δ 3.69 ppm.

3.4. Structure determinations

Suitable crystals were obtained from dichloromethane–petroleum ether at room temperature. Crystal data and details of measurement and refinement are summarized in Table 5. Tables of hydrogen atom coordinates, thermal properties and torsion angles, have been deposited at the Cambridge Crystallographic Data Centre.

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