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Syntheses and Molecular Structures of Pentaphenoxy-2-, 3-, and 4-pyridylmethoxycyclotriphosphazene and their Copper(II) Nitrate Complexes

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ABSTRACT: *The reactions of monochloropentaphenoxycyclotriphosphazene with the sodium salts of 2-, 3-, and 4-pyridylmethanol yield the pentaphenoxy-2-, 3-, and 4-pyridylmethoxycyclotriphosphazenes* **1**, **2**, *and* **3**, *respectively. The X-ray structure analysis of* **1** *shows that the molecule consists of a nearly planar six-membered PN ring. Complexation reactions of* **1**, **2**, *and* **3** *with copper(II) nitrate yield the compounds* $[N_3P_3(OC_6H_5)_5OCH_2(2\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**4**), $[N_3P_3(OC_6H_5)_5OCH_2(3\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**5**), *and* $[N_3P_3(OC_6H_5)_5OCH_2(4\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**6**), *respectively. The molecular structures of* **4** *and* **5** *were determined by X-ray crystallography. Compound* **4** *shows a square-planar geometry around the copper ion with the pyridine nitrogen and one of the nitrate oxygen atoms forming the plane. In* **5**, *the copper ion is octahedrally surrounded by the pyridine nitrogen atoms and two nitrate groups as asymmetrical bidentate chelating ligands.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 9–15, 1999

INTRODUCTION

Polymers with metal-containing groups are of growing interest due to the large range of possible applications for these materials such as ion exchangers, catalysts, electronic conductors, carriers for chemotherapeutical agents, etc. [1–3]. Their coordination chemistry cannot easily be investigated. However, small molecule modeling is a powerful tool to obtain useful information about the chemistry involved in these processes.

The synthesis of phosphazenes with pendent N-donor groups that can form metal complexes with transition elements has attracted considerable attention [1,4]. Cyclo- and polyphosphazenes with pyridine as an N-donor side group have not been systematically investigated, mainly because halogenated phosphazenes are known to form adducts with pyridine derivatives, and these tend to degrade rapidly when water, even in traces, is present in the reaction mixture [5,6].

We recently reported the syntheses and complex formation of pyridylalkylamino-substituted cyclophosphazenes [7–12]. We also described the syntheses, physical properties, and studies on ion uptake of analogous polyphosphazenes [7–9,13]. Interactions of these species with transition metals are possible by N-donor interactions of the pyridinic, amino, and phosphazene nitrogen atoms [8–12]. In the copper nitrate complexes of 2-pyridylmethylamino-substituted cyclotriphosphazenes, the NH group participates in complex formation [11,12], whereas the 3-pyridylmethylamino-substituted compound interacts exclusively with the pyridyl side group

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[8,10]. In both complexes, the copper ion is octahedrally coordinated but with some distortion.

Cyclo- and polyphosphazenes with pendent pyridylalkoxy side groups as N-donor ligands have not yet been investigated, and no molecular structures have been reported. We describe here the syntheses of the first species with 2-, 3-, and 4-pyridylmethoxy-substitution (**1**, **2**, and **3**) and their copper(II) nitrate complexes **4**, **5**, and **6**. The molecular structures of **1**, **4**, and **5** will be discussed.

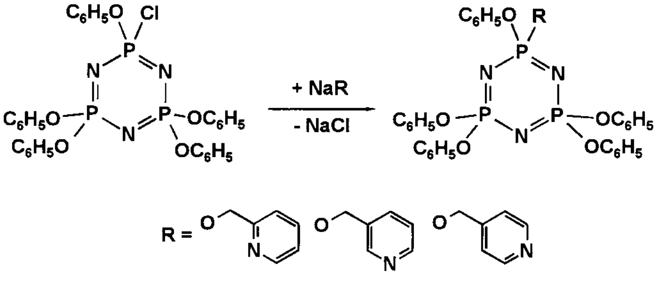
RESULTS AND DISCUSSION

Synthesis and Characterization of Pentaphenoxy-2-, 3-, and 4-pyridylmethoxycyclotriphosphazene (1, 2, and 3)

Monochloropentaphenoxycyclotriphosphazene reacts under rigorously dry conditions with the sodium salts of 2-, 3-, and 4-pyridylmethanol to yield the pentaphenoxy-2-, 3-, and 4-pyridylmethoxycyclotriphosphazenes **1**, **2**, and **3** (Scheme 1). Isolation of **1**, **2**, and **3** was effected by column chromatography, and the compounds were further purified by recrystallization from ether/hexane mixtures.

Evidence for the structures of **1**, **2**, and **3** was obtained by IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, MS, and elemental analyses. The ^{31}P NMR spectra of the three compounds show A_2B patterns with $\delta_A = 10.2$ for the diphenoxy-substituted phosphorus atoms and $\delta_B = 14.1$ (**1**, **3**) and 13.9 (**2**) for the other phosphorus atom ($J_{AB} = 86$ Hz). The IR spectra of the compounds show bands at 1590 and 1490 (CC_{aryl}), 1200–1120 (PN), and 950 cm^{-1} [PO(aryl)]. The CN band of the pyridine group overlaps with the CC band of the phenoxy groups. In addition, the molecular structure of **1** was determined by X-ray crystal structure analysis (Figure 1).

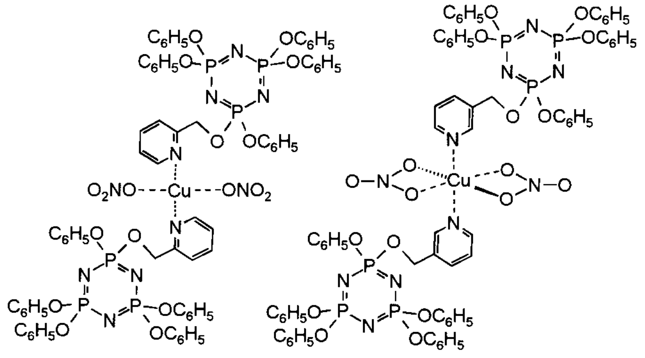
The molecule consists of a nearly planar six-membered PN ring with typical PN distances between 1.56 and 1.58 Å. N-P-N and P-N-P angles are 117° and 122°, respectively. The exocyclic PO bond lengths of 1.56–1.57 Å agree well with published data [14]. Crystal data and collection parameters are listed in Table 1. Selected bond lengths and angles are listed in Table 2.



SCHEME 1

Syntheses and Characterization of the Copper Complexes 4, 5, and 6

Compounds **1**, **2**, and **3** were reacted with copper(II) nitrate in boiling ethanol. After removal of the solvent, each crude product was obtained as a blue oil. Crystallization from diethyl ether was induced and yielded the bright blue crystalline compounds **4**, **5**, and **6**.



4 **5**

$[N_3P_3(OC_6H_5)_5OCH_2(4\text{-}C_5H_4N)]_2Cu(NO_3)_2$

6

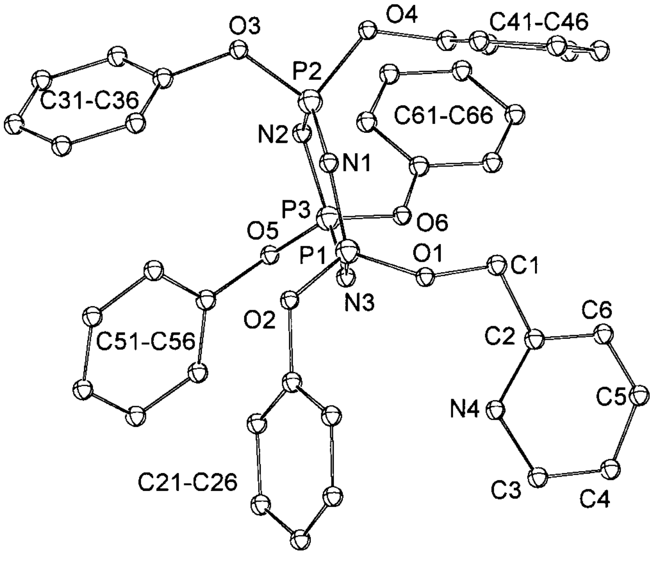


FIGURE 1 The molecular structure and atom-numbering scheme for **1**. Hydrogen atoms are omitted for clarity.

TABLE 1 Crystal Data and Collection Parameters for **1, 4,** and **5**

	1	**4**	**5**
Formula	$C_{36}H_{31}N_4O_6P_3$	$C_{72}H_{62}N_{10}O_{18}P_6Cu$	$C_{72}H_{62}N_{10}O_{18}P_6Cu$
Formula weight	708.56	1604.68	1604.68
Crystal size (mm)	0.67 × 0.10 × 0.15	0.70 × 0.18 × 0.08	0.53 × 0.07 × 0.05
Temperature (K)	293 (2)	293 (2)	293 (2)
Wavelength (Å)	0.7107	0.7107	0.7107
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.50 (1)	9.052 (2)	10.685 (5)
b (Å)	16.855 (3)	11.497 (2)	19.370 (3)
c (Å)	18.077 (4)	19.143 (4)	20.180 (3)
α (°)	90.00 (3)	81.11 (1)	106.76 (1)
β (°)	94.11 (4)	81.67 (2)	104.05 (2)
γ (°)	90.00 (3)	72.14 (2)	104.01 (2)
Volume (Å^3)	3495 (4)	1863.4 (7)	3654 (2)
Z	4	1	2
Density (Mg/m^3)	1.347	1.430	1.459
μ (mm^{-1})	0.222	0.498	0.508
Independent reflns.	4813	5318	6792
Reflections with $I > 2\sigma(I)$	2285	2426	3701
Final $R1$	0.0609	0.0624	0.0509
$wR2$	0.1210	0.1346	0.1012

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for **1**

P1-N1	1.587 (4)	P1-N3	1.563 (4)
P2-N1	1.571 (4)	P2-N2	1.561 (4)
P3-N3	1.579 (4)	P3-N2	1.585 (4)
P1-O1	1.566 (4)	P1-O2	1.575 (4)
P2-O3	1.579 (4)	P2-O4	1.576 (4)
P3-O5	1.565 (4)	P3-O6	1.576 (4)
O1-C1	1.439 (7)	C1-C2	1.484 (9)
C2-C6	1.274 (8)	C2-N4	1.402 (8)
C3-C4	1.34 (1)	C3-N4	1.422 (8)
C4-C5	1.37 (1)	C5-C6	1.27 (1)
N3-P1-N1	117.7 (2)	N2-P2-N1	117.2 (2)
N3-P3-N2	117.1 (2)	P2-N1-P1	122.3 (3)
P2-N2-P3	122.3 (3)	P1-N3-P3	122.2 (2)
O1-P1-N1	111.3 (2)	O2-P1-N1	105.2 (2)
N2-P2-O4	111.9 (2)	N1-P2-O4	110.0 (2)
N2-P2-O3	110.1 (2)	N1-P2-O3	111.6 (2)
N3-P1-O1	109.1 (2)	N3-P1-O2	111.9 (2)
O5-P3-N3	110.5 (2)	O6-P3-N3	106.5 (2)
O5-P3-N2	110.5 (2)	O6-P3-N2	110.9 (2)
O4-P2-O3	93.5 (2)	O5-P3-O6	99.9 (2)
O1-P1-O2	100.2 (2)	C1-O1-P1	121.3 (4)
O1-C1-C2	112.8 (6)	C6-C2-N4	123.6 (6)
C6-C2-C1	116.3 (7)	N4-C2-C1	120.2 (7)
C4-C3-N4	119.7 (8)	C2-N4-C3	115.0 (7)
C3-C4-C5	117.2 (9)	C6-C5-C4	124 (1)
C5-C6-C2	119.6 (8)		

For each compound, characterization by IR spectroscopy shows, besides the bands of the ligand, an additional one at 1380 cm^{-1}, which can be assigned to the NO_3 groups. Additionally, the CN band of **6** shifted to 1620 cm^{-1} due to the interaction of the metal and the pyridine nitrogen atom [15,16]. (+)FAB MS and CHN elemental analyses indicate that all complexes consist of two ligands coordinated to a copper ion.

The structures of **4** and **5** were confirmed by X-ray single-crystal analysis. The results are shown in Figures 2 and 3. Crystal data and collection parameters are listed in Table 1. Selected bond lengths and angles are given in Tables 3 and 4.

In molecule **4,** the geometry around the copper ion (inversion center) is square planar. The pyridine nitrogen and one of the nitrate oxygen atoms form the plane. Bond lengths and angles around copper [Cu–N = 2.014 (6) Å, Cu–O = 1.964 (6) Å and O11-Cu-N4′ = 91.4 (2)°, O11-Cu-N4 = 88.6 (2)°] are in good agreement with other square-planar coordinated copper complexes [17,18]. The bond lengths and angles in the phosphazene ring of **4** are nearly the same as those obtained for **1.**

In complex **5**, the geometry around the copper is octahedral, with a typical distortion. The metal ion is surrounded by two asymmetrically bonded nitrate groups. The copper oxygen distances are between 1.98 and 2.54 Å. The longer Cu–O bond lengths are shorter than the sum of the van der Waals radii of

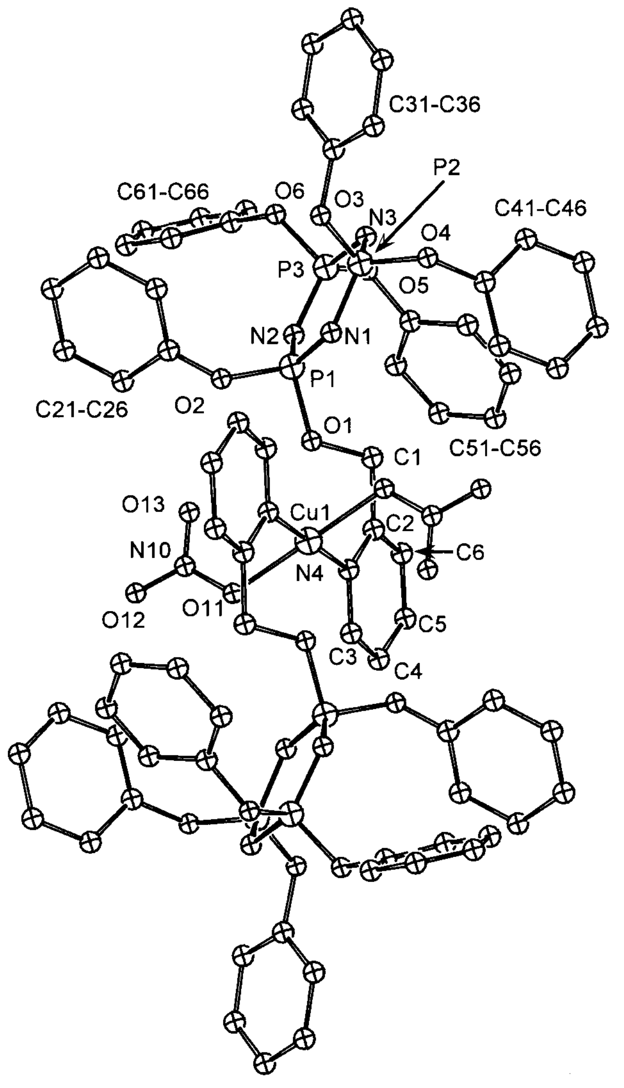


FIGURE 2 The molecular structure and atom-numbering scheme for **4.** Hydrogen atoms are omitted for clarity.

copper (1.4 Å) and oxygen (1.4 Å). The bond angles N-Cu-O are between 87.9° and 93.2° and agree well with published data [17,18].

EXPERIMENTAL

Hexachlorocyclotriphosphazene and monochloropentaphenoxycyclotriphosphazene were synthesized according to standard literature procedures [19,20]. Phosphorus pentachloride, ammonium chloride (Merck), 4-pyridylmethanol (Merck), and copper(II) nitrate [$Cu(NO_3)_2 \cdot 3H_2O$, Riedel de Haen] were used as received. Phenol (Merck) was recrystallized from hexane. 2- and 3-Pyridylmethanol (Merck) were predried over potassium hydroxide and distilled twice before use. Tetrahydrofuran was distilled from benzophenone ketyl. Dichloromethane and hexane were stored over molecular sieves and sodium metal, respectively. Diethyl ether (stabilized for synthesis, Merck) and ethanol (96%, Merck) were used as received. All manipulations were performed under dry argon using standard Schlenk techniques.

^{31}P NMR spectra ($CDCl_3$, 161.7 MHz) were recorded using a Jeol LA 400. ^{13}C and ^{1}H NMR spectra ($CDCl_3$, 62 and 250 MHz) were obtained with a Bruker AM 250-NMR spectrometer. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 (positive chemical shifts downfield). ^{13}C and ^{1}H NMR spectra were referenced to internal standards. IR spectra (**1**, **3**, **4**, **5**, and **6** as KBr pellets; **2** on KBr discs) were measured using a Shimadzu IR-435 IR spectrometer. Elemental analyses were obtained with a Vario EL analyzer. MS were recorded using a spectrometer MAT 711 (Finnigan). (+)FAB spectra were obtained by the use of a CH5 DF spectrometer (Varian MAT).

Preparation of $N_3P_3(OC_6H_5)_5OCH_2(2\text{-}C_5H_4N)$ (**1**)

2-Pyridylmethanol (7.7 g, 0.07 mol) was added slowly to a stirred mixture of sodium (4.38 g, 0.21 mol) and 150 mL of THF. The mixture was then reacted for 12 hours at room temperature. Monochloropentaphenoxycyclotriphosphazene (15.0 g, 0.024 mol) was dissolved in 600 mL of THF. The sodium 2-pyridylmethanolate was added using a double-tipped syringe. The reaction mixture was stirred for 96 hours at room temperature. The solvent was then removed by evaporation. Compound **1** was further purified by column chromatography on aluminum oxide using a 7:3 hexane/dichlormethane mixture as eluent. Recrystallization from a 1:1 hexane/diethyl ether mixture yielded **1** as a white crystalline solid (4.8 g, 28%). Mp 83°C; MS (EI): *m/z* 709 (M^+), 615, 507, 430, 354, 93, 77. Anal. calcd: C, 61.02; H, 4.38; N, 7.91. Found: C, 60.03; H, 4.30; N, 7.43. ^{1}H NMR: 8.5 (d, J = 5.0 Hz, 1H, pyridinic H), 7.6 (t, J = 5.0 Hz), 6.9–7.2 (m, 27H, phenoxy H, 1H, pyridinic H), 4.4 (d, J = 10.0 Hz, 2H, CH_2). ^{13}C-NMR: 151, 129, 125, 121 (phenoxy C), 157, 148, 137, 122 (pyridinic C), 68 (CH_2).

Preparation of $N_3P_3(OC_6H_5)_5OCH_2(3\text{-}C_5H_4N)$ (**2**)

A mixture of sodium (5.4 g, 0.24 mol) in 100 mL of THF was prepared and 3-pyridylmethanol (8.72 g, 0.08 mol) was added carefully. The reaction required about 12 hours for completion. Monochloropentaphenoxycyclotriphosphazene (10.0 g, 0.016 mol) was dissolved in 400 mL of THF. The sodium 3-pyridylmethanolate was added slowly, and the reaction mixture was then stirred for 96 hours at room tempera-

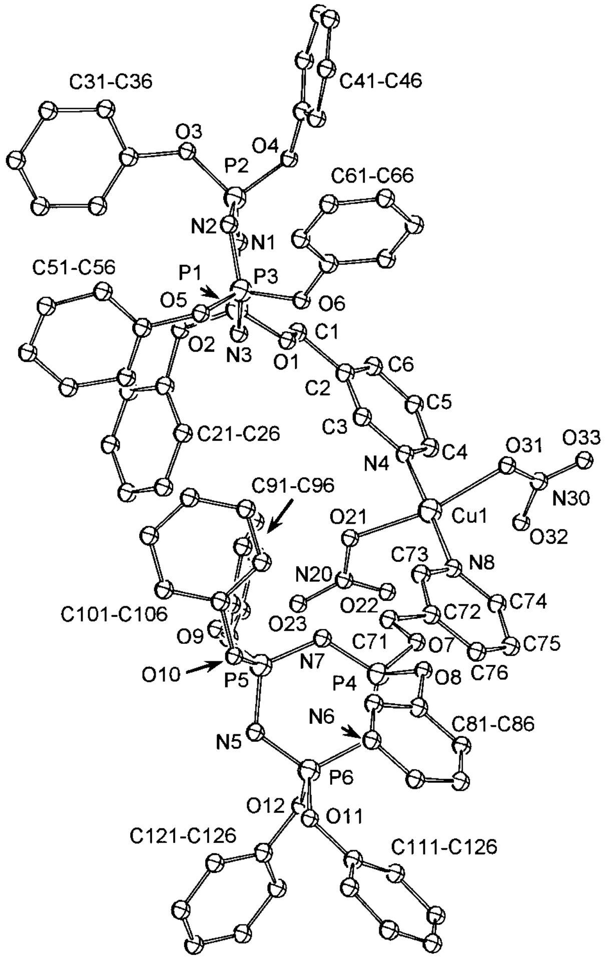


FIGURE 3 The molecular structure and atom-numbering scheme for **5.** Hydrogen atoms are omitted for clarity.

TABLE 3 Selected Bond Lengths (Å) and Angles (°) for **4**

Cu1-O11	1.964 (6)	Cu1-N4	2.014 (6)
P1-N1	1.584 (6)	P1-N2	1.586 (6)
P2-N1	1.569 (6)	P2-N3	1.584 (6)
P3-N2	1.571 (5)	P3-N3	1.574 (6)
P1-O1	1.582 (5)	P1-O2	1.572 (6)
P2-O4	1.579 (5)	P2-O3	1.580 (5)
P3-O6	1.576 (5)	P3-O5	1.584 (5)
O1-C1	1.435 (8)	C1-C2	1.506 (9)
C2-N4	1.348 (9)	C2-C6	1.38 (1)
C3-N4	1.337 (9)	C3-C4	1.38 (1)
C4-C5	1.37 (1)	C5-C6	1.37 (1)
N10-O11	1.234 (8)	N10-O12	1.181 (8)
N10-O13	1.126 (9)		
O11-Cu1-O11′	180.0	N4-Cu1-N4′	180.0
O11-Cu1-N4′	91.4 (2)	O11-Cu1-N4	88.6 (2)
N1-P1-N2	117.4 (3)	N1-P2-N3	117.4 (3)
N2-P3-N3	117.5 (3)	P2-N1-P1	121.4 (4)
P3-N2-P1	122.1 (4)	P3-N3-P2	121.3 (3)
O1-P1-N1	109.5 (3)	O2-P1-N2	112.4 (3)
O1-P1-N2	110.4 (3)	O2-P1-N1	109.1 (4)
N1-P2-O4	111.1 (3)	N1-P2-O3	106.9 (3)
O4-P2-N3	109.4 (3)	O3-P2-N3	111.3 (3)
N2-P3-O6	112.1 (3)	N3-P3-O6	105.7 (3)
N2-P3-O5	109.5 (3)	N3-P3-O5	110.6 (3)
O2-P1-O1	96.0 (3)	O4-P2-O3	99.0 (3)
O6-P3-O5	99.9 (3)	C1-O1-P1	118.7 (4)
O1-C1-C2	108.4 (6)	N4-C2-C6	121.0 (7)
N4-C2-C1	120.2 (8)	C6-C2-C1	118.8 (8)
N4-C3-C4	122.0 (8)	C5-C4-C3	119.6 (8)
C4-C5-C6	118.4 (9)	C5-C6-C2	120.2 (8)
C3-N4-C2	118.9 (7)	O13-N10-O11	115.6 (9)
O12-N10-O11	122.9 (8)	O13-N10-O12	121 (1)

Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z$.

ture. The solvent was removed from the oily brown product by evaporation, and **2** was further purified by column chromatography on aluminum oxide using a 1:4 hexane/dichlormethane mixture. Attempted recrystallization from a 1:1 hexane/diethyl ether mixture yielded **2** as a colorless oil (4.0 g, 35%). MS (EI): *m/z* 708 (M^+), 615, 542, 508, 430, 354, 168, 92. Anal. calcd: C, 61.02; H, 4.38; N, 7.91. Found: C, 60.05; H, 4.37; N, 7.70. ^{1}H NMR: 8.5 (s, 1H, pyridinic H), 7.4 (d, J = 7.0 Hz, 1H, pyridinic H), 6.95–7.35 (m, 1H pyridinic H, 25H phenoxy H), 4.4 (d, J = 8.0 Hz, 2H, CH_2). ^{13}C NMR: 151, 129, 125, 121 (phenoxy C), 149, 148, 134, 124 (pyridinic C), 65 (CH_2).

Preparation of $N_3P_3(OC_6H_5)_5OCH_2(4\text{-}C_5H_4N)$ (**3**)

A solution of monochloropentaphenoxycyclotriphosphazene (7 g, 0.01 mol) in 400 mL of THF was added to a stirred suspension of sodium 4-pyridylmethanolate prepared from small pieces of sodium (5.4 g, 0.24 mol) and 4-pyridylmethanol (3.6 g, 0.033 mol) in 150 mL of THF over a period of 0.5 hour. The mixture was heated to reflux for 24 hours, cooled down to room temperature, and then filtered and centrifuged. The solvent was removed from the oily brown filtrate by evaporation. Further purification of **3** was accomplished by column chromatography on aluminum oxide using diethyl ether as solvent. Recrystallization of the product from a 1:1 hexane/diethyl ether mixture yielded **3** as a white crystalline solid (4.9 g, 69%). Mp 70–72°C; MS (EI): *m/z* 708 (M^+), 615, 601, 539, 522, 431, 355, 168, 93, 66, 39. Anal. calcd: C, 61.02; H, 4.38; N, 7.91. Found: C, 61.0; H, 4.28; N, 7.94. ^{1}H NMR: 8.5 (d, J = 7.2 Hz, 2H, pyridinic H), 7.25–6.9 (m, 25H phenoxy H, 2H pyridinic H), 4.4 (d, J = 10.0 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 151, 129, 125, 121 (phenoxy C) 150, 121 (pyridinic C), 65 (CH_2).

Preparation of $[N_3P_3(OC_6H_5)_5OCH_2(2\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**4**)

Compound **1** (0.22 g, 0.31 mmol) was dissolved in 50 mL of ethanol and then heated to reflux. A solu-

TABLE 4 Selected Bond Lengths (Å) and Angles (°) for **5**

Cu1-N4	1.991 (5)	Cu1-N8	1.997 (5)
Cu1-O21	1.976 (5)	Cu1-O31	2.096 (7)
P1-N1	1.563 (6)	P1-N3	1.579 (6)
P2-N1	1.580 (6)	P2-N2	1.567 (6)
P3-N2	1.573 (6)	P3-N3	1.566 (6)
P1-O1	1.564 (5)	P1-O2	1.599 (6)
P2-O3	1.569 (5)	P2-O4	1.567 (6)
P3-O5	1.556 (6)	P3-O6	1.582 (6)
P4-N6	1.571 (5)	P4-N7	1.567 (5)
P5-N7	1.573 (5)	P5-N5	1.576 (5)
P6-N5	1.562 (5)	P6-N6	1.577 (5)
P4-O7	1.569 (4)	P4-O8	1.595 (5)
P5-O9	1.586 (5)	P5-O10	1.576 (5)
P6-O11	1.570 (5)	P6-O12	1.583 (5)
O1-C1	1.438 (8)	C1-C2	1.501 (9)
C2-C3	1.357 (9)	C2-C6	1.371 (9)
C3-N4	1.347 (8)	N4-C4	1.342 (8)
C4-C5	1.366 (9)	C5-C6	1.35 (1)
O7-C71	1.431 (8)	C71-C72	1.501 (9)
C72-C76	1.372 (9)	C72-C73	1.375 (9)
C73-N8	1.334 (7)	N8-C74	1.317 (8)
C74-C75	1.375 (9)	C75-C76	1.369 (9)
N20-O21	1.293 (8)	N20-O22	1.240 (8)
N20-O23	1.206 (8)	N30-O31	1.162 (8)
N30-O33	1.169 (9)	N30-O32	1.248 (9)
O21-Cu1-N4	89.1 (2)	O21-Cu1-N8	89.3 (2)
N4-Cu1-N8	178.3 (2)	O21-Cu1-O31	164.3 (3)
N4-Cu1-O31	90.3 (2)	N8-Cu1-O31	91.3 (2)
N1-P1-N3	119.0 (3)	N2-P2-N1	117.6 (3)
N3-P3-N2	117.4 (3)	P1-N1-P2	121.0 (4)
P2-N2-P3	121.4 (4)	P3-N3-P1	120.8 (4)
O1-P1-N3	104.9 (3)	N1-P1-O1	111.6 (3)
N1-P1-O2	104.3 (3)	O1-P1-O2	104.2 (3)
N3-P1-O2	112.0 (3)	O4-P2-N2	113.0 (3)
O4-P2-O3	99.2 (3)	N2-P2-O3	109.4 (3)
O4-P2-N1	104.5 (3)	O3-P2-N1	111.5 (3)
O5-P3-N3	109.6 (3)	O5-P3-N2	110.3 (3)
O5-P3-O6	100.1 (4)	N3-P3-O6	106.3 (4)
N2-P3-O6	111.6 (4)	C1-O1-P1	122.0 (5)
O1-C1-C2	107.6 (6)	C3-C2-C6	117.7 (7)
C3-C2-C1	121.6 (7)	C6-C2-C1	120.7 (8)
N4-C3-C2	123.8 (7)	C4-N4-C3	116.9 (6)
N4-C4-C5	122.3 (7)	C6-C5-C4	119.2 (7)
C5-C6-C2	120.0 (8)		
N5-P6-N6	118.3 (3)	N7-P4-N6	115.9 (3)
N7-P5-N5	116.5 (3)	P6-N5-P5	121.9 (3)
P4-N6-P6	121.9 (3)	P4-N7-P5	124.2 (3)
N7-P4-O7	110.4 (3)	O7-P4-N6	111.2 (3)
N7-P4-O8	112.4 (3)	O7-P4-O8	95.7 (3)
N6-P4-O8	109.5 (3)	N7-P5-O10	112.3 (3)
O10-P5-N5	106.5 (3)	N7-P5-O9	109.9 (3)
O10-P5-O9	99.5 (3)	N5-P5-O9	110.9 (3)
N5-P6-O11	104.6 (3)	O11-P6-N6	112.9 (3)
N5-P6-O12	111.1 (3)	O11-P6-O12	104.7 (3)
N6-P6-O12	104.5 (3)	C71-O7-P4	117.8 (4)
O7-C71-C72	110.8 (6)	C76-C72-C73	117.2 (7)
C76-C72-C71	123.9 (7)	C73-C72-C71	118.6 (8)
N8-C73-C72	124.1 (7)	C74-N8-C73	117.3 (6)
N8-C74-C75	123.1 (7)	C76-C75-C74	118.7 (7)
C75-C76-C72	119.7 (7)		
O23-N20-O21	118.5 (9)	O22-N20-O21	116.6 (8)
O23-N20-O22	125.0 (9)	O31-N30-O33	121 (1)
O31-N30-O32	115 (1)	O33-N30-O32	122 (1)

tion of $Cu(NO_3)_2 \cdot 3H_2O$ (0.038 g, 0.157 mmol) in 50 mL of ethanol was added dropwise to the boiling solution. The mixture was heated for 60 minutes. After removal of the solvent, the crude product, a blue oil, was recrystallized from diethyl ether and yielded the pure crystalline bright blue complex **4** (0.02 g, 8%). Mp 92–94°C; MS [(+)FAB]: *m/z* 1479 ($M^+ - NO_3$), 871, 806, 771, 731, 709, 615, 539, 524, 430, 77. Anal. calcd: C, 53.88; H, 3.87; N, 8.73. Found: C, 53.74; H, 3.86; N, 8.51.

Preparation of $[N_3P_3(OC_6H_5)_5OCH_2(3\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**5**)

A mixture of **2** (0.32 g, 0.45 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.054 g, 0.23 mmol) in 50 mL of ethanol was heated to reflux during a period of 2 hours. The mixture was cooled to room temperature and filtered. The pure crystalline product **5** was obtained by removal of the solvent, and crystallization of the bright blue oil from diethyl ether was induced (0.1 g, 14%). Mp 119–122°C; MS [(+)FAB]: *m/z* 1479 ($M^+ - NO_3$), 1450, 1295, 1002, 771, 709, 615, 586, 524, 510, 430, 416, 337, 293, 186, 92, 77. Anal. calcd: C, 53.88; H, 3.87; N, 8.73. Found: C, 54.24; H, 4.00; N, 8.49.

Preparation of $[N_3P_3(OC_6H_5)_5OCH_2(4\text{-}C_5H_4N)]_2Cu(NO_3)_2$ (**6**)

A solution of **3** (0.19 g, 0.27 mmol) in 50 mL of ethanol was added with stirring to $Cu(NO_3)_2 \cdot 3H_2O$ (0.03 g, 0.12 mmol) in 30 mL of ethanol, and the resulting mixture was heated to reflux for 30 minutes. The hot mixture was filtered, and then the filtrate was cooled to room temperature. After removal of the solvent, the crude product, a blue oil, was induced to crystallization from diethyl ether. The complex **6** was obtained as bright blue crystals (0.16 g, 37%). Mp 130°C; MS [(+)FAB]: *m/z* 1480 ($M^+ - NO_3$), 869, 771, 731, 709, 615, 524, 510, 430, 77. Anal. calcd: C, 53.88; H, 3.87; N, 8.73. Found: C, 53.85; H, 4.64; N, 8.35.

Crystal Structure Determination

The single-crystal X-ray intensities were measured at room temperature on a four-circle diffractometer (Enraf-Nonius CAD4) equipped with graphite monochromated Mo K_α radiation. Selected reflections were remeasured periodically during data collection to monitor instrument and crystal stability. Crystal data and technical details of the structure refinements are provided in Table 1. The structures were solved by direct methods (SHELXS-86 [21] for **1** and **4**, SIR-92 [22] for **5**). The final refinements of the structures were performed by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the nonhydrogen atoms, and with hydrogen atoms in calculated positions (SHELXL-93) [23]. No absorption correction was done. The phenyl ring C21-C26 of **4** was fitted to a regular hexagon for better geometrical results.

Additional material regarding the structure determination may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen, Federal Republic of Germany (E-mail: crysdata@FIZ-Karlsruhe.de), referring to the deposition numbers CSD-408559, 408560, and 408561, the names of the authors, and the citation of the present article.

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