

Synthesis of 3-(Aminomethyl)- pyridylpentaphenoxycyclotriphosphazene and its Complex Formation with Copper(II) Nitrate. Molecular Structure of $\{ \text{Cu}[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5(\text{NHCH}_2\text{-}$ $(3\text{-C}_5\text{H}_4\text{N}))]_2(\text{NO}_3)_2 \}$

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Summary. The reaction of monochloropentaphenoxycyclotriphosphazene with 3-(aminomethyl)pyridine yields 3-(aminomethyl)pyridylpentaphenoxycyclotriphosphazene (**1**), a new N-donor ligand with five nitrogen atoms as potential coordination centers. Complex formation with copper(II) nitrate yields compound **2** with the general structure $\text{Cu}(\mathbf{1})_2(\text{NO}_3)_2$. The X-ray structure analysis shows that the copper ion is coordinated by two nitrogen atoms of the pyridine rings and four oxygen atoms of the unsymmetrical bidentate nitrate groups in a *Jahn-Teller* distorted octahedral arrangement.

Keywords. Copper complex; Phosphazene; (Aminomethyl)pyridine; N-Donor ligand.

Synthese von 3-(Aminomethyl)pyridylpentaphenoxycyclotriphosphazen und seine Komplexbildung mit Kupfer(II)nitrat. Molekülstruktur von $\{ \text{Cu}[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5(\text{NHCH}_2(3\text{-C}_5\text{H}_4\text{N}))]_2(\text{NO}_3)_2 \}$

Zusammenfassung. Die Reaktion von Monochlorpentaphenoxycyclotriphosphazen mit 3-(Aminomethyl)pyridin ergibt 3-(Aminomethyl)pyridylpentaphenoxycyclotriphosphazen (**1**), einen neuen N-Donor Liganden mit fünf Stickstoffatomen als potentielle Metallkoordinationszentren. Bei der Umsetzung von **1** mit Kupfer(II)nitrat entsteht der Metallkomplex **2** mit der Zusammensetzung $\text{Cu}(\mathbf{1})_2(\text{NO}_3)_2$. Die durch Röntgenstrukturanalyse ermittelte Molekülstruktur zeigt, daß das Kupferion von zwei Stickstoffatomen der Pyridinringe sowie vier Sauerstoffatomen der unsymmetrisch zweizähligen Nitratgruppen *Jahn-Teller-verzerrt* oktaedrisch umgeben ist.

Introduction

Chlorophosphazenes react with pyridine under formation of cationic adducts. This reaction is often followed by cleavage of the PN bonds of the ring system, predominantly in the presence of water [1, 2]. This might be the reason why pyridine substituted phosphazenes are rarely known. Some of them are only accessible through quite complicated procedures [3–8].

However, we recently reported the straightforward synthesis of cyclo- and polyphosphazenes with pyridine side groups [6–8]. Due to the functional analogy of such new macromolecules to poly(vinylpyridine), a new field of interesting applications can be expected [9–11]. Their chemical properties, especially their coordination behavior, can ideally be investigated by studies of analogue cyclotriphosphazenes as small molecular models [12].

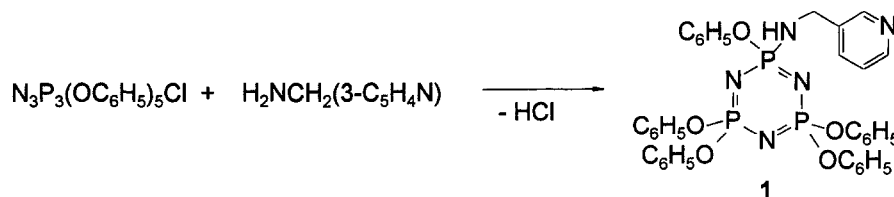
The coordination behavior of phosphazenes with potential N-donor substituents is quite complex. The probability that metal ions will be bonded to the side groups is high when electron withdrawing functional substituents such as pyrazolyl or imidazolyl are combined with cosubstituents which lower the basicity of the PN nitrogen atoms. The same effect has been observed when spacer groups are present between the coordination center and the phosphazene ring [4, 13–17]. In contrast, the attachment of metal ions occurs at the PN nitrogen atoms when electron donating groups such as primary or secondary amines increase the basicity of the ring [18–21]. Intermediate structures where both the nitrogen atoms of the ring and the side groups form a chelating ligand to coordinate the metal are also known [13, 22]. We describe here the synthesis of the first cyclotriphosphazene with 3-(aminomethyl)pyridine as N-donor group (**1**) and its reaction with copper(II) nitrate to form the metal complex **2**.

Results and Discussion

Synthesis and characterization of 3-(aminomethyl)pyridylpentaphenoxycyclotriphosphazene (1)

Monochloropentaphenoxycyclotriphosphazene was reacted with 3-(aminomethyl)pyridine in *THF*; **1** was formed in a clean reaction (Scheme 1). No ring cleavage could be detected following the reaction by ^{31}P NMR spectroscopy.

Isolation of **1** was performed by filtering off the 3-(aminomethyl)pyridine hydrochloride, removing the solvent, and recrystallizing the crude product from ether/hexane.



Scheme 1

The ^{31}P NMR spectrum of **1** shows an A_2B pattern with chemical shifts of $\delta(\text{P}_\text{A}) = 8$ ppm for the purely phenoxy substituted phosphorus atoms and $\delta(\text{P}_\text{B}) = 18$ ppm for that attached to the (aminomethyl)pyridyl group ($J_{\text{AB}} = 77$ Hz).

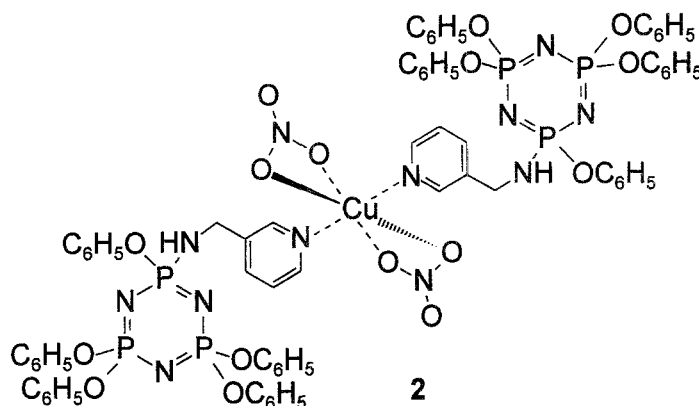
The ^1H NMR spectrum confirms the composition of **1**. The signals for three pyridine protons appear at 8.5 (d, $J = 5$ Hz), 8.3 (s), and 7.2 (d, $J = 6$ Hz) ppm. The

frequencies of the fourth pyridine proton and the protons of the phenoxy groups are in the range of 7.1–8.0 ppm (m). The signal of the methylene protons appears as a *pseudo* triplet (doublet of doublets) at 3.8 ppm ($J = 6$ Hz). A *pseudo* quartet (doublet of triplets) at 2.7 ppm ($J = 6$ Hz) can be assigned to the NH proton.

Three different types of phenoxy groups can be distinguished by ^{13}C NMR spectroscopy: one that is attached geminally to the (aminomethyl)pyridyl group and two which are positioned *cis* and *trans* to the pyridyl substituent relative to the phosphazene ring plane ($\delta = 151, 129, 125, 121$ ppm). The resonance frequencies of the (aminomethyl)pyridyl group can be found at 148 (C2, C6), 135 (C3, C4), 123 (C5), and 42 (methylene C atom) ppm.

Synthesis and characterization of **2**

Copper(II) nitrate and **1** were reacted in boiling methanol. After removal of the solvent, the crude product was obtained as a dark blue powder. Recrystallization from ethanol/methanol mixtures yielded the pure crystalline copper complex **2**.



Characterization by IR spectroscopy shows—besides the vibrations of the ligand—an additional signal at 1380 cm^{-1} which can be assigned to the NO_3 group. FAB MS shows that the complex consists of two ligands coordinated to a copper ion. The final structural proof was achieved by X-ray crystallography. The molecular structure is shown in Fig. 1.

Crystal data and intensity parameters are listed in Table 1. The fractional atomic coordinates are collected in Table 2. Significant bond lengths and angles are shown in Table 3.

The copper ion as the inversion center is bonded to two molecules of **1** by the pyridine N atoms and additionally to four nitrate oxygen atoms in a *Jahn-Teller* distorted octahedral arrangement. The bond distances $\text{Cu-N}(5) = 1.987(3)$, $\text{Cu-O}(61) = 2.082(5)$, and $\text{Cu-O}(62) = 2.299(7)$ Å are in good agreement with other copper(II) nitrate complexes [23]. The appearance of an unsymmetrical bidentate coordination of nitrate groups has been described for several complexes of the

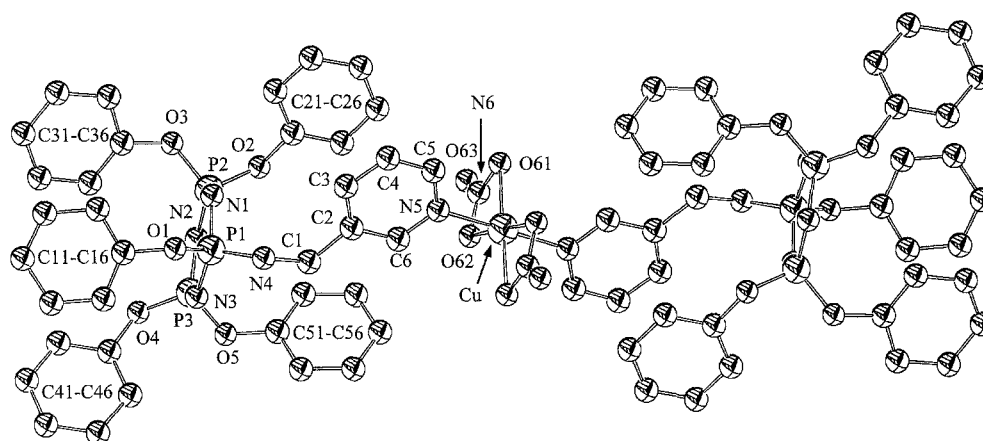


Fig. 1. ORTEP diagram at the 50% probability level of complex **2**; hydrogen atoms have been omitted for clarity

Table 1. Summary of crystal data and intensity collection parameters of **2**

Formula	$C_{72}H_{64}CuN_{12}O_{16}P_6$
Formula weight	1570.94
Crystal size, mm	$0.77 \times 0.07 \times 0.04$
Space group	$P2_1/c$
Crystal system	monoclinic
a (Å)	13.752(3)
b (Å)	13.555(5)
c (Å)	20.657(4)
β (deg)	104.20(2)
V (Å ³)	3733(2)
Z	2
d (calcd.) (g/cm ³)	1.398
θ limits (deg)	$2 < \theta < 25$
μ (cm ⁻¹)	3.58
Radiation (λ , Å)	MoK α , 0.71069
T (K)	293
Scan method	$\omega/2\theta$
Absorption correction type	none
No. of reflections measured	6740
No. of independent reflections	6541
No. of observed reflections	2795
Criterion for observed reflections	$I > 2\sigma(I)$
h	$-15 \rightarrow 16$
k	$-16 \rightarrow 0$
l	$-24 \rightarrow 0$
No. of parameters refined	490
No. of reflections used in refinement	6541
R_{int}	0.0447
R, R_w^*	0.047, 0.108
$(\Delta/\sigma)_{max}$ in last cycle	-2.187
$(\Delta/\rho)_{min}$ (eÅ ⁻³)	-0.463
$(\Delta/\rho)_{max}$ (eÅ ⁻³)	0.372

* $w = 1/[\sigma^2(F_o) + (0.0370 \cdot P)^2 + 0.31 \cdot P]$; $P = \max(F_o^2) + 2F_c^2/3$

Table 2. Atom positions of **2** ($\times 10^4$)

	x	y	z	<i>U</i> (eq)
Cu	5000	5000	0	62(1)
N(6)	5208(4)	6884(5)	150(5)	118(3)
O(61)	5278(3)	6262(5)	591(2)	109(2)
O(62)	4923(4)	3444(6)	428(3)	144(3)
O(63)	5305(4)	7727(5)	276(5)	267(5)
P(1)	10578(1)	5175(1)	2149(1)	38(1)
P(2)	10458(1)	7189(1)	1901(1)	46(1)
P(3)	10346(1)	6500(1)	3130(1)	43(1)
N(1)	10660(2)	6104(2)	1697(2)	41(1)
N(2)	10324(2)	7384(2)	2626(2)	47(1)
N(3)	10492(2)	5434(2)	2881(2)	39(1)
N(4)	9691(2)	4447(2)	1748(2)	46(1)
C(1)	8676(3)	4840(4)	1599(2)	53(1)
C(2)	8082(3)	4707(3)	880(2)	43(1)
C(3)	8507(3)	4512(3)	360(2)	56(1)
C(4)	7894(4)	4434(4)	-274(2)	69(2)
C(5)	6899(4)	4559(4)	-375(2)	68(2)
N(5)	6460(3)	4766(3)	122(2)	56(1)
C(6)	7061(3)	4825(3)	737(2)	50(1)

Table 3. Selected bond lengths (Å) and angles (deg) for **2**

Cu-N(5)	1.987(3)	P(2)-N(1)	1.573(3)
Cu-O(61)	2.082(5)	P(2)-O(2)	1.579(3)
Cu-O(62)	2.299(7)	P(2)-O(3)	1.586(3)
P(1)-O(1)	1.585(3)	P(3)-N(3)	1.563(3)
P(1)-N(3)	1.585(3)	P(3)-N(2)	1.583(3)
P(1)-N(1)	1.588(3)	P(3)-O(5)	1.584(3)
P(1)-N(4)	1.628(3)	P(3)-O(4)	1.586(3)
P(3)-N(2)	1.576(3)		
N(5)#1-Cu-N(5)	180.0	N(3)-P(1)-N(4)	113.4(2)
N(5)-Cu-O(61)#1	88.7(2)	N(1)-P(1)-N(4)	109.5(2)
N(5)-Cu-O(61)	91.3(2)	N(1)-P(2)-N(2)	118.7(2)
O(61)#1-Cu-O(61)	180.0	N(1)-P(2)-O(2)	112.1(2)
N(5)#1-Cu-O(62)	93.1(2)	N(2)-P(2)-O(3)	110.4(2)
N(5)-Cu-O(62)#1	93.1(2)	O(2)-P(2)-O(3)	99.6(2)
O(61)-Cu-O(62)#1	56.8(2)	N(3)-P(3)-N(2)	117.7(2)
O(62)-Cu-O(62)#1	180.0	N(3)-P(3)-O(5)	109.8(2)
O(1)-P(1)-N(3)	109.4(2)	N(2)-P(3)-O(5)	110.4(2)
O(1)-P(1)-N(1)	110.9(2)	N(3)-P(3)-O(4)	113.7(2)
N(3)-P(1)-N(1)	114.7(2)	N(2)-P(3)-O(4)	104.4(2)
P(2)-N(1)-P(1)	122.8(2)	O(5)-P(3)-O(4)	99.1(2)
P(2)-N(2)-P(3)	120.8(2)	O(1)-P(1)-N(4)	97.6(2)
P(3)-N(3)-P(1)	124.4(2)		

Symmetry transformations used to generate equivalent atoms: #1
 $-x + 1, -y + 1, -z$

general formula $[\text{Cu}L_2(\text{NO}_3)_2]$ where L is MeCN, H_2O , pyridine, or 2-methylpyridine [23]. The potential coordination sphere of the amine group directly attached to the phosphazene ring and the PN nitrogen atoms do not participate in the complex formation due to the sterical requirements of the ligand. By contrast, we have shown that the analogues 2-(aminomethyl)pyridine derivative is a chelating ligand with both the nitrogen atoms of the pyridine ring and the amino group or the PN nitrogen atom being bonded to the metal ion [24].

Experimental

Materials

Hexachlorocyclotriphosphazene and monochloropentaphenoxycyclotriphosphazene were synthesized by standard literature procedures [25,26]. Phosphorus pentachloride and ammonium chloride (Merck) were used as received. Phenol (Merck) was recrystallized from pentane. 3-(Aminomethyl)pyridine (Fluka) was predried over potassium hydroxide and distilled onto molecular sieves before use. Copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Riedel de Haen) was used as received. Tetrahydrofuran was distilled from benzophenone ketyl. Methanol and ethanol were distilled and stored over molecular sieves. All manipulations were performed under an atmosphere of dry argon using standard *Schlenk* techniques.

Equipment

^{31}P NMR spectra (36.2 MHz) were recorded using a JEOL FX 90Q spectrometer. ^{13}C and ^1H NMR spectra (62.9 and 250 MHz) were obtained with a Bruker AM 250 NMR spectrometer. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 chemical (positive chemical shifts downfield). ^{13}C and ^1H NMR spectra were referenced to external tetramethylsilane. IR spectra 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 $N_3P_3(\text{OC}_6\text{H}_5)_5(\text{NHCH}_2(3\text{-C}_5\text{H}_4\text{N}))$ (1)

Monochloropentaphenoxycyclotriphosphazene (10.8 g, 0.017 mol) was dissolved in 1.5 l of *THF*. The solution was heated to reflux, and 3-(aminomethyl)pyridine (3.67 g, 0.034 mol) was added slowly to the boiling solution. After heating to reflux for 72 h, the solution was cooled to room temperature. The 3-(aminomethyl)pyridine hydrochloride which precipitated during the reaction was removed by filtration. After removal of the solvent by evaporation, the crude product was recrystallized several times from diethyl ether/hexane (1:1) to yield **1** as a colorless crystalline solid (8.8 g, 73%).

M.p. = 109 °C; MS (EI): m/z 707 (M^+), 614, 600, 520, 508, 432, 414, 353, 184, 122, 92, 77, 65; calcd.: C 61.09, H 4.55, N 9.89; found: C 60.93, H 4.54, N 9.91; IR: 3157 ($\nu\text{-NH}$), 1485 ($\nu\text{-CC}_{\text{aryl}}$), 1220-1120 ($\delta\text{-PN}$), 1020 ($\nu\text{-PO}_{\text{aryl}}$), 765 ($\nu\text{-CH}_{\text{aryl}}$) cm^{-1} .

Preparation of $\{\text{Cu}[N_3P_3(\text{OC}_6\text{H}_5)_5(\text{NHCH}_2(3\text{-C}_5\text{H}_4\text{N}))]_2(\text{NO}_3)_2\}$ (2)

1 (0.4 g, 0.57 mmol) was dissolved in 50 ml methanol and then heated to reflux. A solution of copper(II) nitrate (0.068 g, 0.28 mmol) in 20 ml of methanol was added dropwise to the boiling solution. The mixture was heated for another 15 minutes. After removal of the solvent, the crude product, a dark blue powder, was recrystallized several times from ethanol/methanol (1:1) to yield the pure crystalline complex **2** (0.25 g, 55%).

M.p. = 135 °C; MS ((+)FAB): m/z = 1541 ($\text{M}^+ - \text{NO}_3$), 1478, 897, 861, 832, 770, 708, 614, 600, 508, 414, 217; calcd.: C 53.59, H 4.02, N 10.48; found: C 53.98, H 4.03, N 10.41.

Crystal structure determination

Data were collected using an Enraf Nonius CAD4 diffractometer (293 K, MoK_α -radiation, $\lambda = 0.71069 \text{ \AA}$). Cell dimensions were obtained using 21 well centered reflections with θ in the range of 1–12.5°. The intensities of three reflections chosen as standards were monitored at regular intervals over the course of the data collection. Data were corrected for Lorentz and polarization factors. The structure was solved by direct methods [27]. Refinement of the structure was performed by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms, and with hydrogens in calculated positions [28].

Additional material to the crystal structure determination is available from the authors.

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