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(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 Cu(1)$_2$(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.

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 cyclotriposphazenes 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 cyclotriposphazene with 3-(aminomethyl)pyridine as N-donor group (I) and its reaction with copper(II) nitrate to form the metal complex 2.

Results and Discussion

Synthesis and characterization of 3-(aminomethyl)pyridylpentaphenoxy cyclotriphosphazene (I)

Monochloropentaphenoxy cyclotriphosphazene 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.

The $^{31}$P NMR spectrum of 1 shows an A$_2$B pattern with chemical shifts of $\delta$(PA) = 8 ppm for the purely phenoxy substituted phosphorus atoms and $\delta$(PB) = 18 ppm for that attached to the (aminomethyl)pyridyl group ($J_{AB} = 77$ Hz).

The $^1$H 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