

Syntheses and Crystal Structures of Pentaphenoxy(2-pyridylmethylamino)-cyclotriphosphazene and its Copper(II) Nitrate, Platinum(II) Chloride, and Cobalt(II) Nitrate Complexes

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The reaction of the (2-pyridylmethylamino)-substituted cyclotriphosphazene $N_3P_3(OC_6H_5)_5(NHCH_2(C_5H_4N)-2)$ (**1**) with copper(II) nitrate, platinum(II) chloride, and cobalt(II) nitrate yields the stable complexes $[Cu(NO_3)_2 \cdot (1)_2]$ (**1a**), $[PtCl_2 \cdot (1)]$

(**1b**), $[Co(NO_3)_2 \cdot (1)]$ (**1c**). The X-ray crystallographic studies of these metal complexes revealed the different coordination behavior of the multifunctional ligand.

Since the last decades the interest in polymers which form macromolecular metal complexes has been increasing significantly because of the wide range of possible applications for these materials such as ion exchange resins, catalysts, ionic conductors, and carriers or depots for chemotherapeutic agents^[1–5]. For these applications not only the knowledge of the structures of the metal centers but also the physical properties of the polymeric complexes are important for fundamental mechanistical reasons^[6,7]. Small molecular modelling offers the opportunity to gain important information about the coordination behavior of the functional sites in macromolecules. This method is well established in phosphazene chemistry^[2]. Cyclic phosphazene trimers are, besides their importance in the fundamental research of this class of compounds, indicators for the structural and chemical behavior of analogous macromolecules. Especially the coordination behavior of cyclotriphosphazenes can be studied by X-ray crystallography.

In the past, different side groups which interact with transition metals were described. Previous choices of exocyclic coordination groups include, for example, phosphanes, acetylenic units, or aryl groups^[8,9]. These groups are bound to the metal by P- or π -donor coordination.

Another type of exocyclic side groups are N-donor groups such as pyrazolyl or dimethylamino groups. This kind of phosphazene contains two possible coordination sites which can interact with transition metals: (a) The N-donor side group reacts preferably, when electron-withdrawing groups such as pyrazolyl or imidazolyl are combined with phenyl, phenoxy, or trifluoroethoxy groups^[10–12]. (b) Coordination of the PN nitrogen lone pairs occurs, when primary or secondary amines, which are bound to the phosphazene, increase the basicity of the ring

nitrogen atoms^[1,6,7,12,15]. An intermediate type, where the ring nitrogen atom and the side groups are involved in coordination due to the sterical situation in the molecule, was also described^[16].

Pyridine-substituted phosphazenes are rare, mainly because reactions of chlorinated phosphazenes with pyridine derivatives are known to form cationic adducts which decompose rapidly when water, even in traces, is present in the reaction mixture^[17,18]. Studies of the complex formation of these phosphazene derivatives are hardly known, and no molecular structures of metal complexes have been published so far^[19,20].

We recently described the synthesis of several pyridylalkylamino-substituted cyclo- and polyphosphazenes^[21–23]. 2-(Aminomethyl)pyridine is known to react with transition metal ions as a bidentate chelating ligand^[24]. Once attached to the phosphazene, the three PN nitrogen atoms might additionally participate in complex formation although the possibility of metal interactions at these sites is quite low when cosubstituents lower their basicity.

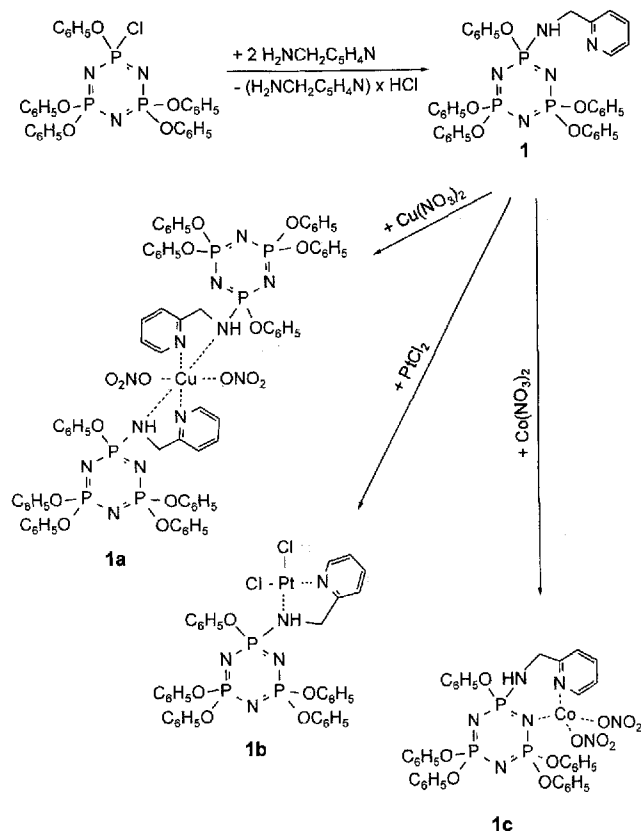
Our latest experiments revealed that the new phosphazene-based N-donor ligand shows a very interesting coordination behavior towards transition metal ions.

In this paper we describe the synthesis and molecular structure of pentaphenoxy(2-pyridylmethylamino)cyclotriphosphazene **1** which is a new multifunctional ligand with five potential N-donor sites. In addition, we succeeded in obtaining metal complexes with copper(II) nitrate **1a**, platinum(II) chloride **1b**, and cobalt(II) nitrate **1c**. The X-ray crystal structure determination of the new compounds shows a rather unexpected coordination behavior of cobalt(II) compared to the expected structures of the copper(II) and platinum complexes **1a** and **1c**. The sterical situ-

ation in platinum complex **1b**, which is a *cis*-platinum derivative, gives rise to the expected potential anticancer activity.

This work is part of a systematic investigation of the coordination behavior of pyridylalkylamino-substituted phosphazenes.

Scheme 1



Results and Discussion

Synthesis and Characterization of Pentaphenoxy-(2-pyridylmethylamino)cyclotriphosphazene **1**

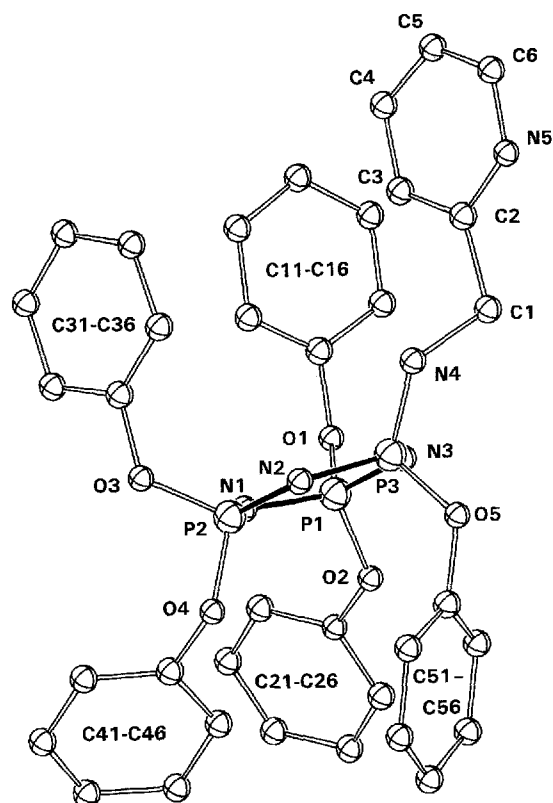
Monochloropentaphenoxy cyclotriphosphazene, $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)_5\text{Cl}$, reacts with rigorous exclusion of moisture with 2-(aminomethyl)pyridine to yield pentaphenoxy(2-pyridylmethylamino)cyclotriphosphazene **1**. No decomposition or degradation of the PN ring system could be detected by monitoring the reaction by ^{31}P -NMR spectroscopy.

The structure of **1** was determined by IR, ^1H -, ^{13}C -, and ^{31}P -NMR spectroscopy, MS and EA. The IR spectrum of **1** shows bands at 3260 cm^{-1} (NH), 1580 , 1476 (CC_{aryl}), 1216 – 1112 (PN), 940 (PO_{aryl}), the CN band of the pyridyl group overlaps with the CC band of the phenoxy groups.

Additionally, the molecular structure was determined by X-ray structure crystallography.

Crystal data and data collection parameters are listed in Table 1. The P–N bond lengths within the P_3N_3 ring lie in a narrow range [$1.562(3)$ – $1.605(3)$ Å], which is typical of cyclotriphosphazenes^[13,25]. The exocyclic P–N bond length

Figure 1. ORTEP diagram of **1** at the 50% probability level of the repeating unit; the hydrogen atoms have been omitted for clarity^[a]



[a] Selected bond lengths [Å] and angles [°]: P(1)–N(3) 1.569(3), P(1)–O(2) 1.574(3), P(1)–O(1) 1.577(3), P(1)–N(1) 1.591(3), P(2)–N(1) 1.562(3), P(2)–N(2) 1.575(3), P(2)–O(3) 1.584(3), P(2)–O(4) 1.591(3), P(3)–N(3) 1.580(3), P(3)–O(5) 1.604(3), P(3)–N(2) 1.605(3), P(3)–N(4) 1.623(3); N(3)–P(1)–O(2) 107.4(2), N(3)–P(1)–O(1) 109.9(2), O(2)–P(1)–O(1) 98.8(2), N(3)–P(1)–N(1) 118.0(2), O(2)–P(1)–N(1) 110.5(2), O(1)–P(1)–N(1) 110.6(2), N(1)–P(2)–N(2) 116.9(2), N(1)–P(2)–O(3) 109.3(2), N(2)–P(2)–O(3) 111.1(2), N(1)–P(2)–O(4) 112.7(2), N(2)–P(2)–O(4) 107.0(2), O(3)–P(2)–O(4) 98.4(2), N(3)–P(3)–O(5) 109.3(2), N(3)–P(3)–N(2) 116.2(2), O(5)–P(3)–N(2) 107.4(2), N(3)–P(3)–N(4) 110.0(2), O(5)–P(3)–N(4) 104.2(2), N(2)–P(3)–N(4) 109.1(2), P(2)–N(1)–P(1) 121.0(2), P(2)–N(2)–P(3) 122.9(2), P(1)–N(3)–P(3) 122.0(2).

is longer [$1.623(3)$ Å], indicating less double bond character. The exocyclic angles at the phosphorus atoms differ considerably: $[\text{O}(1)–\text{P}(1)–\text{O}(2)$ $98.8(2)^\circ$, $\text{O}(5)–\text{P}(3)–\text{N}(4)$ $104.2(2)^\circ$, $\text{O}(3)–\text{P}(2)–\text{O}(4)$ $98.4(2)^\circ$]. The difference of 5.6° at the pyridyl-substituted phosphorus atom can be attributed to the relative orientation of the phenoxy and pyridyl groups^[26]. The phosphazene ring is almost planar.

Synthesis and Characterization of the Metal Complexes

Synthesis and Characterization of the Copper Complex **1a**

The reaction of **1** with copper(II) nitrate in boiling methanol yields $[\text{Cu}(\text{NO}_3)_2 \cdot (\text{1})_2]$ **1a**.

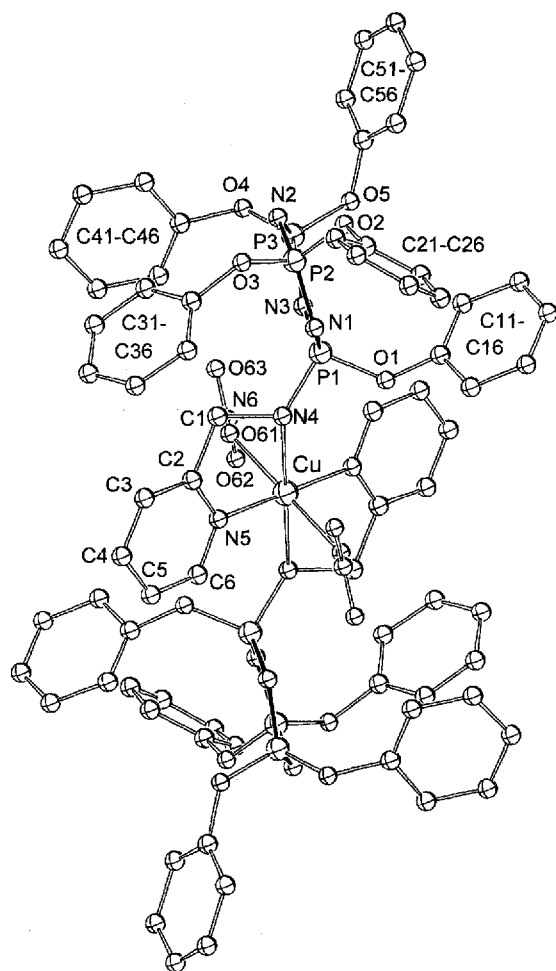
The IR spectrum of **1a** shows besides the bands, which can also be found in the spectrum of the ligand, two additional bands at 1380 and 1610 cm^{-1} assigned to the nitrate group and the CN group of the pyridine ring. These bands have been shifted to higher wavenumbers due to the

interaction between the metal and the pyridine nitrogen atom^[27,28].

(+)FAB MS and CHN elemental analysis indicate that the complex consists of two ligands coordinated to a copper ion.

The final structure of **1a** was confirmed by single-crystal X-ray diffraction (Figure 2).

Figure 2. ORTEP diagram at the 50% probability level of the repeating unit found in complex **1a**; the hydrogen atoms have been omitted for clarity^[a]



^[a] Selected bond lengths [Å] and angles [°]: Cu(1)–N(5) 1.962(7), Cu(1)–N(4) 2.638(7), Cu(1)–O(61) 1.985(6), P(1)–N(3) 1.580(7), P(1)–O(1) 1.583(6), P(1)–N(1) 1.595(7), P(1)–N(4) 1.654(7), P(2)–N(2) 1.566(7), P(2)–O(3) 1.570(6), P(2)–O(2) 1.582(6), P(2)–N(1) 1.595(7), P(3)–O(5) 1.566(6), P(3)–O(4) 1.569(6), P(3)–N(2) 1.571(7), P(3)–N(3) 1.591(7); N(5)–Cu(1)–O(61) 91.0(3), N(4)–Cu(1)–N(5) 90.0(3), N(4)–Cu(1)–O(61) 90.0(3), N(3)–P(1)–O(1) 112.3(3), N(3)–P(1)–N(1) 115.2(3), O(1)–P(1)–N(1) 109.9(3), N(3)–P(1)–N(4) 108.1(3), O(1)–P(1)–N(4) 95.4(3), N(1)–P(1)–N(4) 114.4(4), N(2)–P(2)–O(3) 110.6(3), N(2)–P(2)–O(2) 106.4(3), O(3)–P(2)–O(2) 99.0(3), N(2)–P(2)–N(1) 116.4(3), O(3)–P(2)–N(1) 110.3(3), O(2)–P(2)–N(1) 112.7(3), O(5)–P(3)–O(4) 100.1(3), O(5)–P(3)–N(2) 113.0(3), O(4)–P(3)–N(2) 109.0(3), O(5)–P(3)–N(3) 105.7(3), O(4)–P(3)–N(3) 110.5(3), N(2)–P(3)–N(3) 117.2(3), P(1)–N(1)–P(2) 124.1(4), P(2)–N(2)–P(3) 121.5(4), P(1)–N(3)–P(3) 122.0(4).

Crystal data and collection parameters are listed in Table 1. The geometry around the copper as inversion center is octahedral, with a typical Jahn-Teller distortion. The two

pyridine N atoms and the two oxygen atoms of the nitrate groups form a regular plane with atomic distances of Cu(1)–N(5) 1.962(7) Å and Cu(1)–O(61) 1.985(6) Å. The atomic distance between the metal and the amine nitrogen atom [2.63(3) Å] is smaller than the sum of van der Waals radii of Cu (1.4 Å) and N (1.5 Å). All bond lengths are typical of d⁹ copper complexes and agree with published data^[29,30]. The exocyclic P–N bond length of the metal complex is slightly longer (0.031 Å) compared to ligand **1**. The PN ring bond lengths in **1a** vary over a narrow range [1.566(7)–1.595(7) Å] and are close to those of the ligand.

Synthesis and Characterization of the Platinum Complex **1b**

The platinum complex **1b** is formed during the reaction of **1** with platinum(II) chloride in chloroform/benzene mixtures. It was isolated in 20% yield. The (+)FAB MS data of the reaction products revealed the formation of a second metal complex of the composition [PtCl₂ · (1)]. In addition, other not yet identified products could be detected by ³¹P-NMR spectroscopy.

The CHN elemental analysis and the (+)FAB MS of crystalline **1b** show a ligand-to-metal ratio of 1:1. The IR spectrum is similar to that of **1** with the exception of a characteristic shift of the CN band to higher wavenumbers (1608 cm^{−1}).

Figure 3 shows the X-ray crystal structure of **1b**.

Crystal data and collection parameters are listed in Table 1. The geometry of **1b** is almost square-planar. The Pt–N [1.99(3) and 2.14(2) Å] and the Pt–Cl [2.2(1) Å] bond lengths are nearly the same. The Cl–Pt–Cl angle is 90.3(3)°, while the N–Pt–N angle is smaller [83(1)°], which can be attributed to considerable strain caused by the bidentate ligand. Similar deformations around platinum atoms were observed in other five-membered chelated ring systems and our data agree well with published data^[31]. The exocyclic P–N bond length [1.70(2) Å] is much longer than observed for the ligand **1** which is obviously a result of the decreased double bond character caused by localization of the nitrogen electron lone pair due to complex formation. The PN ring bond lengths vary from 1.50(2) to 1.62(3) Å and are close to those of **1**.

Compound **1b** is of significant interest as a potential anticancer drug. Its geometry is analogous to that of the *cis*-platinum and the sterical situation around the platinum will probably allow an attack at the DNA nitrogen bases.

Synthesis and Characterization of the Cobalt Complex **1c**

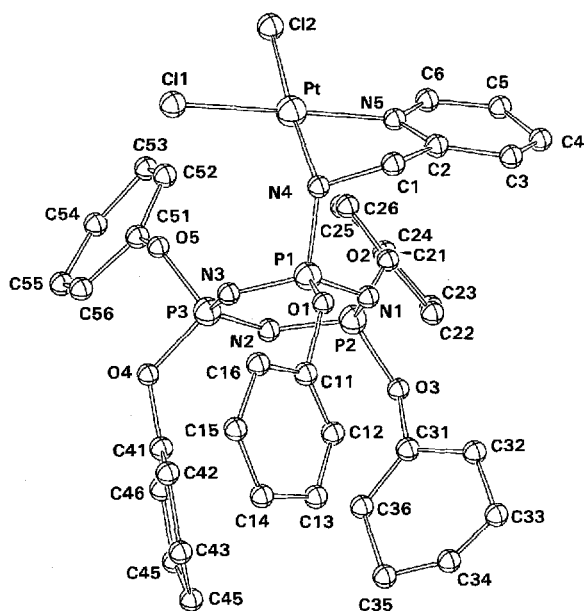
The cobalt complex **1c** was prepared by reaction of **1** with cobalt(II) nitrate in boiling ethanol. Single crystals were obtained from a mixture of ethylbenzene and ethanol.

The IR spectrum of **1c** shows compared to that of **1** additional band at 1380 cm^{−1} for the NO₃ group and at 1608 cm^{−1} for the pyridine CN which interacts with the cobalt ion.

The CHN elemental analysis and the (+)FAB MS indicate a ratio of metal to ligand of 1:1.

In contrast to the copper and platinum complexes **1a** and **1b**, the coordination type of the cobalt(II) nitrate complex

Figure 3. ORTEP diagram at the 50% probability level of the repeating unit found in complex **1b**; the hydrogen atoms have been omitted for clarity^[a]



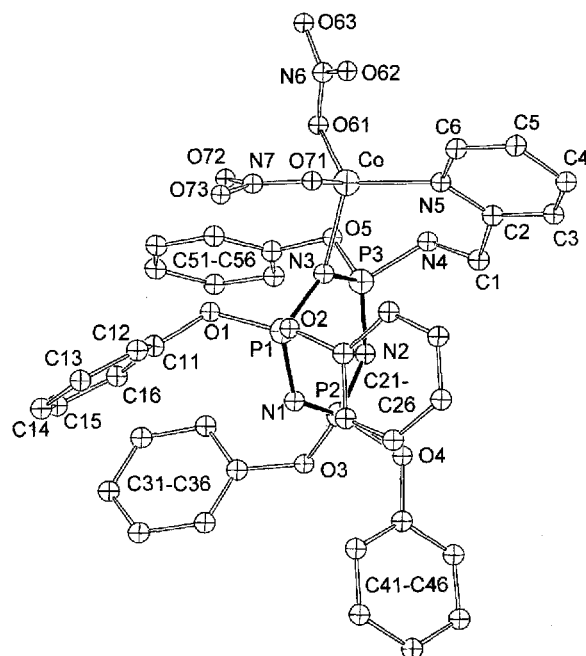
^[a] Selected bond lengths [Å] and angles [°]: Pt(1)–N(5) 1.99(3), Pt(1)–N(4) 2.14(2), Pt(1)–Cl(2) 2.27(8), Pt(1)–Cl(1) 2.29(7), P(2)–O(2) 1.57(2), P(2)–N(1) 1.57(2), P(2)–O(3) 1.56(2), P(2)–N(2) 1.62(3), P(1)–N(3) 1.50(2), P(1)–O(1) 1.56(2), P(1)–N(1) 1.55(2), P(1)–N(4) 1.70(2), P(3)–O(5) 1.52(2), P(3)–N(3) 1.60(3), P(3)–N(2) 1.62(3), P(3)–O(4) 1.62(2); N(5)–Pt(1)–N(4) 82.5(12), N(5)–Pt(1)–Cl(2) 93.3(11), N(4)–Pt(1)–Cl(2) 175.6(7), N(5)–Pt(1)–Cl(1) 175.9(11), N(4)–Pt(1)–Cl(1) 93.9(6), Cl(2)–Pt(1)–Cl(1) 90.3(3), O(2)–P(2)–N(1) 108.7(11), O(2)–P(2)–O(3) 100.4(11), N(1)–P(2)–O(3) 111.1(11), O(2)–P(2)–N(2) 107.7(11), N(1)–P(2)–N(2) 118.1(13), O(3)–P(2)–N(2) 109.2(13), N(3)–P(1)–O(1) 110.1(12), N(3)–P(1)–N(1) 118.8(13), O(1)–P(1)–N(1) 111.6(11), N(3)–P(1)–N(4) 112.4(13), O(1)–P(1)–N(4) 93.1(10), N(1)–P(1)–N(4) 107.9(11), O(5)–P(3)–N(3) 108.1(12), O(5)–P(3)–N(2) 112.1(12), N(3)–P(3)–N(2) 117.8(14), O(5)–P(3)–O(4) 97.4(12), N(3)–P(3)–O(4) 110.8(13), N(2)–P(3)–O(4) 108.9(12), P(1)–N(1)–P(2) 123(2), P(3)–N(2)–P(2) 118(2), P(1)–N(3)–P(3) 122(2).

1c is rather unusual (Figure 4). One of the PN ring nitrogen atoms and the nitrogen atom of the pyridyl side group are involved in the coordination to the metal, although the skeleton bears slightly electron-withdrawing substituents so that the PN ring nitrogen atoms should be poor donors.

The geometry around the cobalt ion is distorted tetrahedral. The Co(1)–N(5), Co(1)–N(3) and Co(1)–O(61), Co(1)–O(71) bond lengths are in good agreement with those in other cobalt(II) nitrate complexes with N-donor ligands^[29,32].

The ring bond length P(3)–N(3) [1.65(1) Å] is much longer and the exocyclic P–N bond lengths are slightly shorter (0.02 Å) than those found for the analogous bonds of **1**. These findings can be attributed to a reduction of the electron density in the phosphazene ring and to an increased delocalization of the nitrogen lone pair of the amino group. Several structural studies of cyclophosphazene ligands show the same phenomena^[16].

Figure 4. ORTEP diagram at the 50% probability level of the repeating unit found in complex **1c**; the hydrogen atoms have been omitted for clarity^[a]



^[a] Selected bond lengths [Å] and angles [°]: Co(1)–O(61) 2.011(10), Co(1)–N(5) 2.033(13), Co(1)–O(71) 2.036(9), Co(1)–N(3) 2.077(9), P(1)–O(1) 1.543(9), P(1)–N(1) 1.549(9), P(1)–O(2) 1.569(8), P(1)–N(3) 1.589(10), P(3)–N(2) 1.551(10), P(3)–O(5) 1.564(10), P(3)–N(4) 1.591(11), P(3)–N(3) 1.647(10), P(2)–O(3) 1.557(9), P(2)–O(4) 1.575(10), P(2)–N(2) 1.576(11), P(2)–N(1) 1.587(11); O(61)–Co(1)–N(5) 119.7(4), O(61)–Co(1)–O(71) 126.1(5), N(5)–Co(1)–O(71) 93.4(5), O(61)–Co(1)–N(3) 102.7(4), N(5)–Co(1)–N(3) 109.2(4), O(71)–Co(1)–N(3) 104.5(4), O(1)–P(1)–N(1) 111.3(5), O(1)–P(1)–O(2) 101.4(4), N(1)–P(1)–O(2) 111.0(5), O(1)–P(1)–N(3) 105.7(5), N(1)–P(1)–N(3) 116.9(5), O(2)–P(1)–N(3) 109.2(5), N(2)–P(3)–O(5) 110.6(5), N(2)–P(3)–N(4) 118.1(6), O(5)–P(3)–N(4) 96.6(5), N(2)–P(3)–N(3) 113.4(5), O(5)–P(3)–N(3) 113.0(5), N(4)–P(3)–N(3) 104.0(5), O(3)–P(2)–O(4) 99.8(5), O(3)–P(2)–N(2) 113.2(5), O(4)–P(2)–N(2) 104.6(6), O(3)–P(2)–N(1) 109.8(5), O(4)–P(2)–N(1) 112.2(5), N(2)–P(2)–N(1) 116.0(5), P(1)–N(1)–P(2) 123.1(6), P(3)–N(2)–P(2) 26.1(6), P(1)–N(3)–P(3) 122.2(6), P(1)–N(3)–Co(1) 131.3(5), P(3)–N(3)–Co(1) 106.4(5).

Conclusion

Pentaphenoxy(2-pyridylmethylamino)cyclotriphosphazene **1** was synthesized and completely characterized. Its molecular structure was determined by X-ray crystallography. **1** is a multifunctional N-donor ligand with five potential N-donor sites. Reactions of **1** with copper(II) nitrate and platinum(II) chloride yielded compounds with metal-to-ligand ratios of 1:2 (**1a**) and 1:1 (**1b**), where only the nitrogen atoms of the pyridylmethylamino groups participate in the complex formation. In contrast, the molecular structure determination of the cobalt(II) nitrate complex **1c** revealed a different situation, where one of the P–N ring nitrogen atoms and the pyridyl N atom are bound to the metal center.

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Table I. Crystal data and structure refinement for **1**, **1a**, **1b**, and **1c**

	1	1a	1b	1c
Formula	C ₃₆ H ₃₂ N ₅ O ₅ P ₃	C ₇₂ H ₆₄ N ₁₂ O ₁₆ P ₆ Cu	C ₃₆ H ₃₂ Cl ₂ N ₅ O ₅ P ₃ Pt	C ₃₆ H ₃₂ N ₇ O ₁₁ P ₃ Co
Formula Weight	707.00	1602.71	973.57	890.53
Crystal Size [mm]	0.02 x 0.08 x 0.75	0.3 x 0.35 x 0.15	0.05 x 0.025 x 0.75	0.7 x 0.3 x 0.25
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.7107	0.7107	0.7107	0.7107
Space Group	P2 ₁ /c	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$
Crystal System	monoclinic	triclinic	monoclinic	triclinic
a [Å]	9.663(3)	9.79(2)	17.985(2)	10.36(2)
b [Å]	17.202(3)	11.90(1)	9.604(2)	14.25(1)
c [Å]	20.950(5)	17.62(2)	25.123(3)	14.315(7)
α [°]		97.93(9)		76.96(5)
β [°]	102.00(2)	98.4(1)	101.000(9)	68.14(9)
γ [°]		97.4(1)		88.5(1)
Volume [Å ³]	3406(2)	1987(5)	4260(1)	1907(4)
Z	4	1	4	2
Density [Mg/m ³]	1.380	1.339	1.518	1.551
μ [mm ⁻¹]	0.226	0.466	3.58	0.647
Reflections obsd.	6338	3874	5797	3843
Independent reflns.	5961	3709	5658	3564
Final R	R1 = 0.0456,	R1 = 0.0587,	R1 = 0.0772,	R1 = 0.0688,
[I > 2 σ (I)]	wR2 = 0.1164	wR2 = 0.1543	wR2 = 0.2316	wR2 = 0.1632

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Experimental

General: The solvents were dried by heating at reflux with the appropriate drying agents: THF and diethyl ether were distilled from sodium/benzophenone. Benzene, hexane, and ethyl benzene were stored over sodium metal. Methanol and chloroform were distilled and stored over molecular sieves. – Hexachlorocyclotriphosphazene and monochloropentaphenoxycyclotriphosphazene were synthesized according to literature procedures^[33,34]. 2-(Aminomethyl)pyridine (Fluka) was predried over potassium hydroxide and distilled before use. Cu(NO₃)₂ · 3 H₂O, Co(NO₃)₂ · 6 H₂O, and PtCl₂ (Merck) were used as received. – The synthesis of **1** was carried out under dry argon by using standard Schlenk techniques. – Infrared spectra: Shimadzu IR-435 spectrophotometer, KBr pellets. – ¹H- and ¹³C-NMR spectra: Bruker AM 250-NMR spectrometer, internal standard TMS. – ³¹P-NMR spectra: Jeol FX 90Q spectrometer, 36.23 MHz, external standard 85% H₃PO₄. – Elemental analyses: Vario EL (Elementar). – MS (80 eV): MAT 711 (Finnigan) spectrometer; (+)FAB MS spectra: Varian MAT spectrometer.

X-ray Crystallography and Data Collection^[35]: The crystals were mounted on an Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo-K α radiation (λ = 0.7107 Å). The intensity data were collected by using the $\omega/2\theta$ scan mode in the range Θ = 2–25°. Three standard reflections were used to check the changes in orientation of the crystal. – **Structure Solution and Refinement**: The structures were solved by the Patterson heavy-atom method using SHELXS-76 (for **1b**) or by direct methods and by subsequent difference Fourier syntheses using SHELXS-76. The scattering factors for H, C, N, P, O, Cl, and the metals were those included in the above programs. For the final refinement the SHELXL-93 program^[36] was used. Refinement of the structure was carried out according to the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated and refined once isotropically. The crystal data and final refinement parameters are also given in Table I.

Synthesis of Pentaphenoxy(2-pyridylmethylamino)cyclotriphosphazene (1): 2-(Aminomethyl)pyridine (1.02 g, 9.6 mmol) was added dropwise to a solution of N₃P₃(OC₆H₅)₃Cl (3 g, 4.71 mmol) in 250 ml THF. The reaction mixture was heated at reflux for 40 h. It was then cooled down to room temp. and filtered to remove the precipitated 2-(aminomethyl)pyridine hydrochloride. The solvent was removed from the solution and the remaining yellow oil was dried in vacuo and then recrystallized from an diethyl ether/hexane (1:1) mixture. A white solid was obtained (2.6 g, 78%, m.p.: 82°C). Single crystals could be obtained after recrystallization from hexane. – MS (EI) [M(**1**) = 707]; *m/z*: 707 [M⁺], 614, 508, 414, 354, 307, 184, 107, 77. – C₃₆H₃₂N₅O₅P₃ (707.0): calcd. C 61.10, H 4.52, N 9.90; found C 60.99, H 4.81, N 10.01. – ³¹P NMR (CDCl₃): A₂B, δ (P_A) = 8, δ (P_B) = 18, J_{AB} = 76.9 Hz. – ¹H NMR (CDCl₃): δ = 8.5 [d, J = 5.0 Hz, 1H, pyridinic H], 7.6 [t, J = 7.5 Hz, 1H, pyridinic H], 6.9–7.2 [m, 5H, phenoxy H, 2H, pyridinic H], 3.9 [d of d, J_{NHCH} = 7.5 Hz, J_{CHP} = 10.0 Hz, 2H, CH₂], 3.7 [m, 1H, NH]. – ¹³C NMR (CDCl₃): δ = 151, 129, 125, 120 [s, 4C, phenoxy C], 158, 148, 136, 121 [s, 4 C, pyridinic C], 45 [s, 1 C, CH₂].

Synthesis of [Cu(NO₃)₂ · (1)] (1a): Cu(NO₃)₂ · 3 H₂O (120.8 mg, 0.5 mmol) in 20 ml ethanol was heated at reflux. A solution of **1** (353.8 mg, 0.5 mmol) in 40 ml ethanol was added dropwise. The solution was concentrated to 5 ml in vacuo. Blue crystals were obtained after several days (200 mg, 25%, m.p.: 91°C). – (+)FAB MS [M(**1a**) = 1602.7]; *m/z*: 1541 [M + H⁺ – NO₃]⁺, 1478, 859, 832, 770, 708, 600. – C₇₂H₆₄N₁₂O₁₆P₆ (1602.7): calcd. C 53.54, H 3.96, N 10.41; found C 52.95, H 4.4, N 10.12.

Synthesis of [PtCl₂ · (1)] (1b): A solution of **1** (0.26 g, 0.37 mmol) in 10 ml of a mixture of benzene/CHCl₃ (1:1) was added dropwise to a heated solution of PtCl₂ (0.1 g, 0.37 mmol) in 10 ml of a benzene/CHCl₃ (1:1) mixture. The solution was heated at reflux for 15 min. It was then cooled down and filtered off to remove an insoluble residue. After concentration pale yellow crystals were obtained. (72 mg, 20%, m.p.: 190°C). – (+)FAB MS [M(**1b**) = 973.1]; *m/z*: 974 [M + H⁺], 938, 901, 708, 600, 507, 383, 307, 217, 154, 107, 77. – C₃₆H₃₂Cl₂N₅O₅P₃Pt (973.6): calcd. C 44.39, H 3.28, N 7.19; found C 44.61, H 3.65, N 6.98.

Synthesis of $[Co(NO_3)_2 \cdot (1)]$ (1c): A solution of $Co(NO_3)_2 \cdot 6 H_2O$ (145.5 mg, 0.5 mmol) in 40 ml of ethanol and was heated at reflux. A solution of **1** (353.8 mg, 0.5 mmol) in 40 ml of ethanol was added dropwise. After the reaction mixture had been concentrated in vacuo to about 10 ml a violet solid precipitated. Crystals could be obtained after recrystallization from an ethyl benzene/ethanol mixture (1:1) (120 mg, 27%, m.p.: 150 °C). – (+)FAB MS $[M(1c) = 890.04]$; m/z : 828 $[M + H^+ - NO_3]$, 765, 708, 689, 614, 508, 414. – $C_{36}H_{32}CoN_7O_{11}P_3$ (890.5): calcd. C 48.54, H 3.59, N 11.01; found C 48.61, H 3.81, N 10.89.

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