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Article

Di- and Trinuclear Complexes Derived from Hexakis(2-pyridyloxy)cyclotriphosphazene. Unusual P–O Bond Cleavage in the Formation of $[\{(L'CuCl)_2(Co(NO_3)\}Cl]$ ($L' = N_3P_3(OC_5H_4N)_5(O)$)

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Hexakis(2-pyridyloxy)cyclotriphosphazene (**L**) is an efficient multisite coordination ligand which binds with transition metal ions to produce dinuclear (homo- and heterometallic) complexes $[L(CuCl)(CoCl_3)]$, $[L(CuCl)(ZnCl_3)]$, $[L(CoCl)(ZnCl_3)]$, and $[L(ZnCl_2)_2]$. In these dinuclear derivatives the cyclophosphazene ligand utilizes from five to six nitrogen coordination sites out of the maximum of nine available sites. Further, the spacer oxygen that separates the pyridyl moiety from the cyclophosphazene ring ensures minimum steric strain to the cyclophosphazene ring upon coordination. This is reflected in the near planarity of the cyclophosphazene ring in all the dinuclear derivatives. In the dinuclear heterobimetallic derivatives one of the metal ions [Cu(II) or Co(II)] is hexacoordinate and is bound by the cyclophosphazene in a η^5-gem-N_5 mode. The other metal ion in these heterobimetallic derivatives [Co(II) or Zn(II)] is tetracoordinate and is bound in an η^1-N_1 fashion. In the homobimetallic derivative, $[L(ZnCl_2)_2]$, one of the zinc ions is five-coordinate (η^3-nongem-N_3), while the other zinc ion is tetracoordinate(η^2-gem-N_2). The reaction of **L** with $CuCl_2$ followed by $Co(NO_3)_2{\cdot}6H_2O$ yields a trinuclear heterobimetallic complex $[\{(L'CuCl)_2Co(NO_3)\}Cl]$ [$L' = N_3P_3(OC_5H_4N)_5(O)$]. In the formation of this compound an unusual P–O bond cleavage involving one of the phosphorus–pyridyloxy bonds is observed. The molecular structure of $[\{(L'CuCl)_2Co(NO_3)\}Cl]$ [$L' = N_3P_3(OC_5H_4N)_5(O)$] reveals that each of the two the P–O-cleaved L′ ligands is involved in binding to Cu(II) to generate the motif L′CuCl. Two such units are bridged by a Co(II) ion. The coordination environment around the bridging Co(II) ion contains four oxygen (two P–O units, one chelating nitrate) and two nitrogen atoms (pyridyloxy nitrogens).

Introduction

The rich nucleophilic substitution chemistry of chlorocyclophosphazenes and the relative robustness of the cyclophosphazene framework have allowed the use of these inorganic P–N heterocyclic rings as suitable scaffolds for the construction of multisite coordination ligands.[1] Many different types of cyclophosphazene-based ligands have been designed and utilized to prepare coordination and organometallic compounds.[2−8] A further interest in these ligands comes from the ability to readily extend the small molecule chemistry to appropriate high polymers such as the corresponding polyphosphazenes or polymers that contain cyclophosphazenes as pendant groups.[9] We have recently demonstrated a successful application of this principle by studying the pyrazolyl cyclophosphazenes as ligands[10] and later translating the small molecule chemistry to the assembly

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of copper- and palladium-metalated cyclophosphazene-containing polymers.[11] The latter were shown to be versatile recyclable phosphoesterases (copper-containing polymers)[11a] or recyclable catalysts for the Heck reaction (palladium-containing polymers).[11b] In view of this, we have been interested in the metalation behavior of other cyclophosphazene-based multisite coordination ligands. Although the ligand hexakis(2-pyridyloxy)cyclophosphazene (**L**) was reported earlier,[5a] the multisite binding behavior of this ligand has only been recently demonstrated.[12] Herein, we report the versatility of **L** for the assembly of a variety of dinuclear (homo- and heterobimetallic) derivatives, [L(CuCl)(CoCl$_3$)] (**1**), [L(CuCl)(ZnCl$_3$)] (**2**), [L(CoCl)(ZnCl$_3$)] (**3**), and [L(ZnCl$_2$)$_2$] (**4**). Ligand **L** shows a remarkable and diverse metal-dictated coordination response in these bimetallic complexes: η^5-gem-N$_5$, η^3-nongem-N$_3$, η^2-gem-N$_2$, and η^1-N$_1$. Remarkably, the reaction of **L** with CuCl$_2$ followed by Co(NO$_3$)$_2$·6H$_2$O leads to the formation of a trinuclear heterobimetallic compound [{(L′CuCl)$_2$(Co(NO$_3$)}Cl] (**5**) (L′ = N$_3$P$_3$(OC$_5$H$_4$N)$_5$(O)). Compound **5** contains two cyclophosphazene-based ligands, each of which binds to Cu(II) in a η^5-gem-N$_5$ mode analogous to that observed in compounds **1**−**3**. However, from the remaining portion of the multisite coordination ligand one of the pyridyloxy units is hydrolyzed to yield a P−O unit. Two such in situ-generated metallo ligands bind to Co(II) in a η^2-gem-N,O manner. The coordination environment around Co(II) is completed by a chelating nitrate ligand.

Experimental Section

General Methods. Solvents and other general reagents used in this work were purified according to standard procedures. Hexachlorocyclotriphosphazene (Nippon Soda, Japan) was recrystallized from *n*-hexane before use. Anhydrous cobalt(II) chloride, copper(II) chloride, zinc(II) chloride (Fluka, Switzerland), 2-hydroxy pyridine (Lancaster, U.K.), and cobalt(II) nitrate hexahydrate (S. D. Fine, India) were used as received. Hexakis(2-pyridyloxy)cyclotriphosphazene (**L**) was prepared according to the procedure reported in the literature.[5a]

Instrumentation. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL spectrometer operating at 400.0 and 161.7 MHz, respectively. Chemical shifts are reported with respect to internal tetramethylsilane (^{1}H) and external 85% H$_3$PO$_4$ (^{31}P). Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. Electronic spectra were recorded on Perkin-Elmer-Lambda 20 UV−vis spectrometer and on a Shimadzu UV-160 spectrometer using CH$_3$CN as the solvent. Solid-state electronic spectra were obtained on Nujol mulls adhered to Whatman filter paper strips. EPR spectra were recorded on a Bruker EMX 1444 X-band EPR spectrometer (fitted with a quartz dewar for measurements up to 120 K). The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH (g = 2.0037). Magnetic susceptibility measurement was carried out by SQUID (superconducting quantum interference device) using a Quantum Design magnetic property measurement system XL (U.S.A.) at 300 K and corrected for the magnetization of the sample holder and capsule and the diamagnetic contribution to the samples, which were estimated from Pascal's constants.[13] Solution electrical conductivity measurements (25 °C) were carried out using an Elico (India) type CM-82 T conductivity bridge. Elemental analyses of the compounds were obtained on a Thermoquest CE instruments CHNS−O, EA/110 model.

X-ray Crystallography. Suitable crystals for **1**−**3** and **5** were obtained by slow evaporation of their dichloromethane solutions. Suitable crystals of **4** were obtained by slow diffusion of *n*-hexane into its dichloromethane solution. The crystal data for compounds **1**−**5** were collected on a Bruker SMART APEX CCD diffractometer. The program SMART (version 6.45) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction. The crystal structures were solved and refined by full-matrix least-squares methods against F^2 using the program SHELXTL (version 6.14).[14] All non-hydrogen

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Table 1. Crystal and Structure Refinement Data for Compounds **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{33}H_{30}Cl_{10}CoCuN_9O_7P_3$	$C_{33}H_{32}Cl_{10}CuZnN_9O_7P_3$	$C_{33}H_{32}Cl_{10}CoZnN_9O_7P_3$
fw	1234.54	1243.00	1238.39
temp	100(2)	100(2)	100(2)
wavelength	0.71073	0.71073	0.71073
cryst syst	triclinic,	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions	$a = 12.3851(8)$ Å $b = 14.4997(9)$ Å $c = 15.9015(10)$ Å $\alpha = 114.3990(10)°$ $\beta = 108.646010)°$ $\gamma = 96.5650(10)°$	$a = 12.3771(8)$ Å $b = 14.5180(10)$ Å $c = 15.8869(11)$ Å $\alpha = 114.4740(10)°$ $\beta = 108.7240(10)°$ $\gamma = 96.4470(10)°$	$a = 12.4411(7)$ Å $b = 14.4689(8)$ Å $c = 15.9762(9)$ Å $\alpha = 114.7440(10)°$ $\beta = 109.4440(10)°$ $\gamma = 95.7290(10)°$
vol, Z	2361.5(3), 2	2359.0(3), 2	2364.9(2), 2
density (cald)	1.736	1.750	1.739
abs coeff	1.525	1.683	1.580
F(000)	1236	1246	1242
cryst size	0.2 × 0.3 × 0.2	0.1 × 0.2 × 0.1	0.2 × 0.1 × 0.2
θ range	2.30−28.31	2.55−28.32	2.06−28.32
limiting indices	$-16 \leq h \leq 14$ $-14 \leq k \leq 19$ $-20 \leq l \leq 21$	$-16 \leq h \leq 10$ $-19 \leq k \leq 19$ $-19 \leq l \leq 21$	$-16 \leq h \leq 16$ $-19 \leq k \leq 16$ $-17 \leq l \leq 21$
reflns collected	15 909	15 843	15 910
independent reflns	11 252 ($R_{int} = 0.0163$)	11 241 ($R_{int} = 0.0189$)	11 266 ($R_{int} = 0.0192$)
completeness to θ	28.31	28.32	28.32
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	11 252/0/577	12 141/0/585	11 266/0/577
GOF on F^2	1.039	1.040	1.041
final R indices [$I > 2\sigma(I)$]	R1 = 0.0459, wR2 = 0.1131	R1 = 0.0505, wR2 = 0.1380	R1 = 0.0522, wR2 = 0.1386
R indices (all data)	R1 = 0.0506, wR2 = 0.1163	R1 = 0.0581, wR2 = 0.1432	R1 = 0.0605, wR2 = 0.1444
largest diff. peak and hole	1.900 and −1.360	1.844 and −1.575	1.744 and −1.316

atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. The crystal data for **1**−**3** are given in Table 1, and those for **4** and **5** are given in Table 2. The program SQUEEZE[15] in PLATON[16] was used to remove the severely disordered *n*-hexane solvent molecule in the lattice of **4**.

Synthesis. Synthesis of the Dinuclear Heterobimetallic Complexes 1−3. The general procedure for the preparation of these metal complexes is as follows. The metal chloride (M_aCl_2) (0.2 mmol) was added to a solution of the ligand **L** (0.2 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 2 h at room temperature. At this stage, the second metal chloride (M_bCl_2) (0.2 mmol) was added, and the reaction mixture was stirred for a further 12 h at room temperature. Filtration, followed by removal of the solvent from the filtrate, yielded heterobimetallic complexes **1**−**3**. These were purified by recrystallization from slow evaporation of their dichloromethane solutions to give [L(CuCl)(CoCl$_3$)](**1**), [L(CuCl)(ZnCl$_3$)] (**2**), and [L(CoCl)(ZnCl$_3$)] (**3**) The characterization data for these compounds are given below.

[L(CuCl)(CoCl$_3$)]·3CH$_2$Cl$_2$·H$_2$O (1). Yield: 0.155 g (72%). mp: 130 °C (d). IR (KBr): ν 3419 (b), 3058 (m), 1601 (m), 1469 (s), 1434 (s), 1302 (sh), 1211 (s), 1150 (sh), 1051 (s), 964 (s), 898 (s), 781 (m), 625 (m), 530 (s), 466 cm^{-1} (sh). UV−vis (CH$_3$CN): λ_{max} (ϵ_{max}) 861 (39), 684 (427), 661 (354) (sh), 588 (303), 462 nm (128 M^{-1} cm^{-1}). Solid-state UV−vis: λ_{max} 675, 537, 419 nm. Room-temperature magnetic moment (after applying diamagnetic corrections): 4.75 μ_B. MS (FAB): 793 [L(CoCl)]$^+$; 797 [L(CuCl)]$^+$. Anal. Calcd for $C_{33}H_{32}Cl_{10}Co_1Cu_1N_9O_7P_3$: C, 32.05; H, 2.60; N, 10.19. Found: C, 31.90; H, 2.55; N, 10.08.

[L(CuCl)(ZnCl$_3$)]·3CH$_2$Cl$_2$·H$_2$O (2). Yield: 0.160 g (82%). mp: 142 °C (d). IR (KBr): ν 3357 (b), 3058 (m), 1602 (m), 1470 (s), 1434 (s), 1303 (s), 1210 (s), 1201 (s), 1149 (s), 1103 (sh), 1053 (s), 966 (s), 902 (s), 828 (sh), 781 (s), 739 (sh), 619 (m), 530 (s), 468 cm^{-1} (s). UV−vis (CH$_3$CN): λ_{max} (ϵ_{max}) 788 nm (29 M^{-1} cm^{-1}). Solid-state UV−vis: λ_{max} 754 nm. Room-temperature magnetic moment (after applying diamagnetic corrections): 1.85 μ_B. MS (FAB): 797 [L(CuCl)]$^+$. Anal. Calcd for $C_{33}H_{32}Cl_{10}Cu_1Zn_1N_9O_7P_3$: C, 31.88; H, 2.59; N, 10.19. Found: C, 32.08; H, 2.35; N, 10.31.

[L(CoCl)(ZnCl$_3$)]·3CH$_2$Cl$_2$·H$_2$O (3). Yield: 0.171 g (80%). mp: 155 °C (d). IR (KBr): ν 3362 (b), 3057(m), 2926 (sh), 1645 (sh), 1601 (s),1573 (sh), 1470 (s), 1434 (s), 1305 (sh), 1215 (sh), 1205 (s),1198 (b), 1054 (s), 964 (b), 900 (s), 782 (s), 627 (m), 531 (s), 475 (s), 434 cm^{-1} (sh). UV−vis (CH$_3$CN): λ_{max} (ϵ_{max}) 688 (7) (sh), 588 (20), 553 (17) (sh), 513 (13) (sh), 471 nm (12 M^{-1} cm^{-1}). Solid-state UV−vis: λ_{max} 582 nm. Room-temperature magnetic moment (after applying diamagnetic corrections): 4.25 μ_B. MS (FAB): 793 [L(CoCl)]$^+$. Anal. Calcd for $C_{33}H_{32}Cl_{10}Cu_1Zn_1N_9O_7P_3$: C, 32.00; H, 2.60; N, 10.18. Found: C, 31.78; H, 2.35; N, 10.10.

Synthesis of [L(ZnCl$_2$)$_2$] (4). ZnCl$_2$ (0.4 mmol) was added to a solution of **L** (0.2 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 12 h at room temperature. It was then filtered, and the solvent was removed from the filtrate to yield **4** which was purified by crystallization by diffusing *n*-hexane into its dichloromethane solution. Yield: 0.130 g (67%). mp: 110 °C (d). ^{1}H NMR (CDCl$_3$): δ 8.22 (m), 7.66 (m), 7.09 (m), 6.96 (m). ^{31}P NMR (CDCl$_3$): δ 5.09 (s). IR (KBr): ν 3065 (b), 1646 (sh),

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Table 2. Crystal and Structure Refinement Data for Compounds **4** and **5**

	4	**5**
empirical formula	$C_{30}H_{24}N_9O_6P_3Zn_2Cl_4$	$C_{53}H_{46}Cl_9Co_1Cu_2N_{17}O_{16}P_6$
fw	972.08	1867.97
temp	100(2)	100(2)
wavelength	0.71069	0.71073
cryst syst	orthorhombic,	orthorhombic
space group	*Pbca*	*Fddd*
unit cell dimensions	$a = 18.964(5)$ Å $b = 14.599(5)$ Å $c = 32.075(5)$ Å	22.6394(18) Å 28.2017(18) Å 45.260(4) Å
vol, *Z*	8880(4), 8	28897(4), 18
density (calcd)	1.454	1.653
abs coeff	1.477	1.563
F(000)	3904	14 528
cryst size	0.1 × 0.1 × 0.1	0.2 × 0.1 × 0.2
θ range	2.15−28.32°	2.01−28.30°
limiting indices	$-25 \leq h \leq 19$ $-19 \leq k \leq 18$ $-27 \leq l \leq 42$	$-30 \leq h \leq 30$ $-20 \leq k \leq 37$ $-53 \leq l \leq 60$
reflns collected	56 911	47 065
independent reflns	11 051 ($R_{int} = 0.1645$)	8972 ($R_{int} = 0.0458$)
completeness to θ	28.32	28.30
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	11 051/0/487	8972/0/492
GOF on F^2	0.966	1.027
final R indices [$I > 2\sigma(I)$]	R1 = 0.0840 wR2 = 0.1741	R1 = 0.0598 wR2 = 0.1787
R indices (all data)	R1 = 0.1696 wR2 = 0.2056	R1 = 0.0755 wR2 = 0.1787
largest diff. peak and hole	2. 506 and −1.211	1.207 and −1.676

1602 (s),1539 (sh), 1471 (s), 1434 (s), 1301 (s), 1220 (s), 1210 (sh), 1112 (s), 1053 (s), 949 (s), 896 (s), 781 (s), 732 (sh), 626 (sh), 594 (sh), 537 (sh),512 (sh), 434 cm^{-1} (sh). MS (FAB): 803 [L(ZnCl)]$^+$. Anal. Calcd for $C_{38}H_{24}Cl_4Zn_2N_9O_6P_3$: C, 39.32; H, 2.40; N, 12.50. Found: C, 40.98; H, 2.35; N, 11.68.

Synthesis of [{(L′CuCl)$_2$(Co(NO$_3$)}Cl]·3CH$_2$Cl$_2$·H$_2$O (5). $CuCl_2$ (0.2 mmol) was added to a solution of **L** (0.2 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for 2 h at room temperature. At this stage, the $Co(NO_3)_2$•$6H_2O$ (0.2 mmol) was added, and the reaction mixture was stirred for a further 12 h at room temperature. Filtration was followed by concentration of the filtrate to about 20 mL. This was allowed to crystallize at room temperature to give **5**. Yield: 36 mg (22%). mp: 210 °C (d). IR (KBr): ν 3446 (b), 3105 (m), 1604 (s), 1471 (s), 1436 (s), 1295 (s), 1225 (s), 1140 (s), 1050 (sh), 951 (s), 905 (sh), 863 (sh), 785 (s), 734 (sh), 606 (sh), 549 (m), 468 cm^{-1} (s). Solid-state UV−vis: λ_{max} 837, 674, 474, 415, 315 nm. Room-temperature magnetic moment (after applying diamagnetic corrections): 5.61 μ_B. MS (FAB): 780 [L′CuCoCl]$^+$, 841 [L′CuCoCl(NO$_3$)]$^+$, 1499 [L′$_2$Cu$_2$CoCl$_2$]$^+$, 1561 [L′$_2$Cu$_2$CoCl$_2$(NO$_3$)]$^+$. Anal. Calcd for $C_{53}H_{46}Cl_9Cu_2Co_1N_{17}O_{16}P_6$: C, 34.07; H, 2.48; N, 12.74. Found: C, 33.60; H, 2.39; N, 12.51.

Results and Discussion

Synthetic and Spectroscopic Aspects. Sequential metalation of **L** with anhydrous metal chlorides in a 1:1 stoichiometry produced the heterobimetallic complexes [L(CuCl)(CoCl$_3$)] (**1**), [L(CuCl)(ZnCl$_3$)] (**2**), and [L(CoCl)(ZnCl$_3$)] (**3**). The dinuclear homometallic complex [L(ZnCl$_2$)$_2$] (**4**) was prepared by a 1:2 reaction of **L** with anhydrous zinc chloride (Scheme 1), the metalation of **L** with anhydrous copper chloride in a 1:1 stoichiometry, followed by reaction with $Co(NO_3)_2$•$6H_2O$, produced the trinulear heterobimetallic compound [{(L′CuCl)$_2$(Co(NO$_3$)}Cl] (**5**) (L′ = $N_3P_3(OC_5H_4N)_5(O)$) in a modest yield (22%) (Scheme 2). We were unable to isolate any other pure products in this reaction. The formation of **5** involves an unusual P−O bond cleavage reaction. Although P−O bond cleavage reactions in phosphate ester hydrolysis are well documented in synthetic systems, most of these involve activated substrates containing a *p*-nitrophenolate substituent.[11a,17] There have been no prior examples of P−O bond hydrolysis reactions in cyclophosphazene ligands, although earlier studies on pyrazolyl cyclophosphazenes, as well as acyclic phosphorus pyrazolides, have revealed the hydrolytic susceptibility of the P−N bond.[10c,18] It is of interest to note that Ainscough and co-workers reported the formation of a trinuclear derivative [L$_2$Cu$_3$Cl$_4$][Cu$_2$Cl$_6$] in a 2:5 reaction of **L** with $CuCl_2$.[12a] However, unlike in the present case, the ligand remained intact. To the best of our knowledge, **5** represents the first trinuclear heterobimetallic derivative prepared from **L**. FAB mass spectra of **1**−**4** did not show a molecular ion peak; however, several prominent fragment ion peaks {viz., [L(CoCl)]$^+$ *m/e* 793, 100%, [L(CuCl)]$^+$ *m/e* 797, 89% (**1**); [L(CuCl)]$^+$ *m/e* 797, 100% (**2**); [L(CoCl)]$^+$ *m/e* 793, 100% (**3**); [L(ZnCl)]$^+$ *m/e* 803, 50% (**4**)} were detected. But the FAB mass spectra of **5** reveals that the trinuclear core survives mass spectral conditions: [L′CuCoCl]$^+$ 780 (63%), [L′CuCoCl(NO$_3$)]$^+$ 841 (38%), [L′$_2$Cu$_2$CoCl$_2$]$^+$ 1499 (31%), and [L′$_2$Cu$_2$CoCl$_2$(NO$_3$)]$^+$ 1561 (20%). Compounds **1**−**4** are nonionic in solution and do not show any prominent conductivity in their acetonitrile solutions. This indicates that, in solution, the chloride ligands are also bound to the metal ion as is found in the solid state (vide infra). Conductivity measurements of **5** could not be carried out because of its poor solubility.

Compound **1** displays a broad d−d band at 861 nm in solution, characteristic of an elongated rhombic octahedral coordination environment around copper(II).[12b] Interestingly the corresponding d−d band in **2** is shifted to 788 nm. Other strong absorptions in **1** occur at 684, 588, and 661 nm and are indicative of a cobalt(II) present in the distorted tetrahedral arrangement.[19] In addition, a peak at 462 nm is

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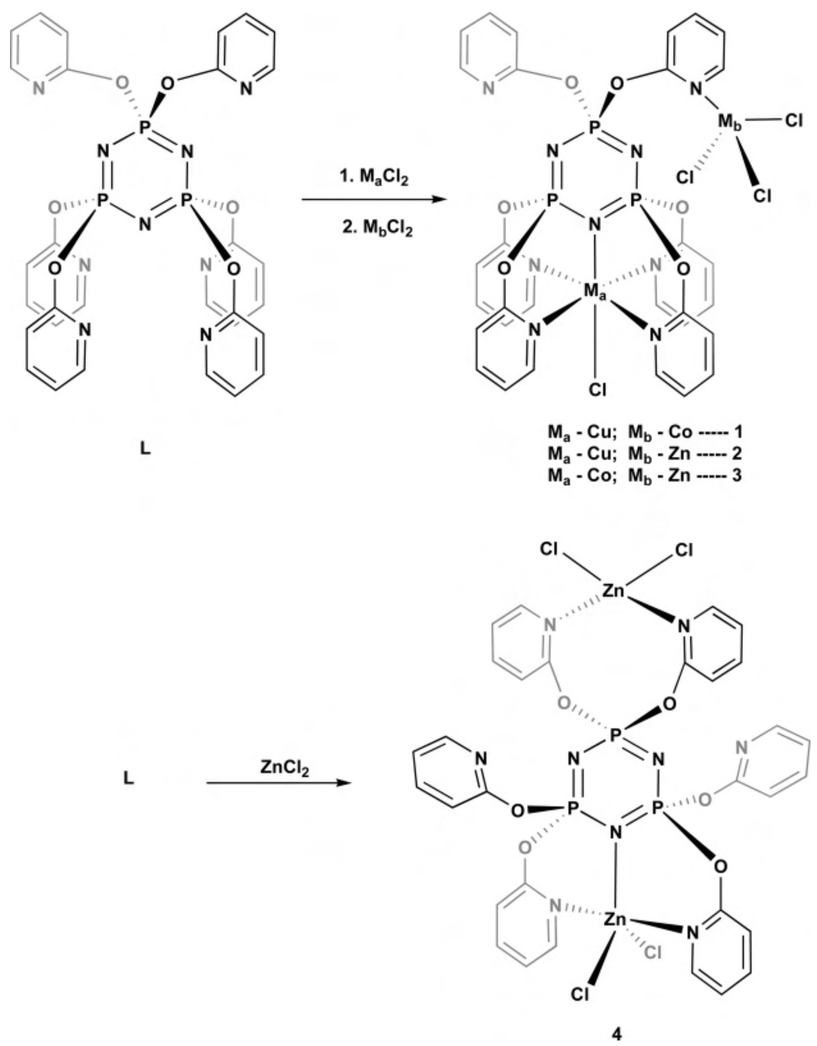
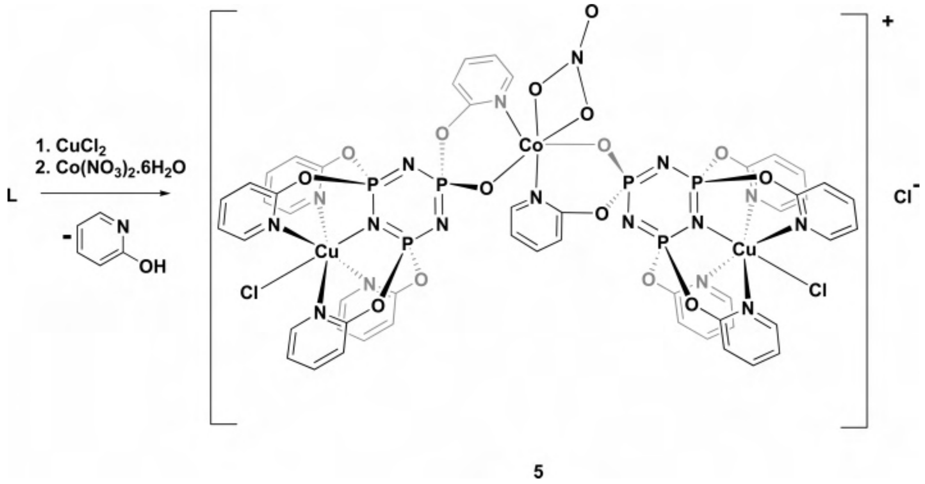
Scheme 1



Scheme 2



observed and assigned to the Cl → M LMCT band.[10a,12b] The electronic spectrum of **3** shows prominent d−d bands at 688 and 588 nm with shoulders at 553 and 513 nm. These come from the cobalt(II) present in a distorted octahedral coordination environment.[19] A strong peak at 417 nm is observed and is attributed to the Cl → M LMCT.[10a,12b] The electronic spectrum of compound **5** could be carried out in its solid-state only because of its poor solubility. However, absorption maxima were detected at 837 [Cu(II)], 674, 474, 315 [Co(II)], and 415 nm (Cl → M LMCT). [10a,12b]

The EPR spectra of complexes **1** and **2** in their polycrystalline states display an unresolved axial $S = 1/2$ spectrum [$g_{\perp} = 2.13$, $g_{\parallel} = 2.48$ (**1**) and $g_{\perp} = 2.13$, $g_{\parallel} = 2.55$ (**2**)] at room temperature. The nature of the spectrum did not vary even when the temperature was lowered to 120 K [$g_{\perp} = 2.14$, $g_{\parallel} = 2.53$ (**1**) and $g_{\perp} = 2.12$, $g_{\parallel} = 2.45$ (**2**)]. However, the spectra of these compounds recorded in dichloromethane–toluene glass (120 K) revealed a typical resolved axial Cu(II) species with a four-line pattern in the parallel region ($g_{\parallel} = 2.31$, $A_{\parallel} = 124 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.07$ for compound **1**).[20] For compound **2** these values are $g_{\parallel} = 2.30$, $A_{\parallel} = 130 \times 10^{-4}$ cm^{-1}, and $g_{\perp} = 2.08$) (see Supporting Information for EPR spectra of **1** and **2**). It is interesting to note that in [$L_2Cu_3Cl_4$][Cu_2Cl_6] and [LCuCl]PF_6, reported by Ainscough et al., these values are $g_{\parallel} = 2.40$, $A_{\parallel} = 123 \times 10^{-4}$ cm^{-1}, $g_{\parallel} = 2.42$, and $A_{\parallel} = 158 \times 10^{-4}$ cm^{-1} and $g_{\parallel} = 2.42$, $g_{\perp} = 2.17$, and $A_{\parallel} = 159 \times 10^{-4}$ cm^{-1}, respectively.[12a,12b] The EPR spectrum of **5** in its polycrystalline state displays an isotropic signal ($g = 2.15$) at room temperature, and the nature of the spectrum did not vary even when the temperature was lowered to 120 K ($g = 2.16$). For **1** and **2**, the g values obtained are greater than 2.0 and $g_{\parallel} > g_{\perp}$, indicating a $d_{x^2-y^2}$ ground state.[21] We were unable to obtain any clear EPR signals resulting from Co(II) in **1** or for **3** (both in solution and solid-state, even at 120 K), presumably because of relaxation. Such behavior had been noted earlier for mixed metal-ion clusters containing Co(II).[22] However, magnetic studies on **1**, **3**, and **5** support the presence of Co(II). Thus, the room-temperature magnetic moment value of complex **1** is 4.75 μ_B (spin-only $\mu_B = 4.90$ μ_B) consistent with the presence of a Cu(II) and a high-spin Co(II) in this complex. The magnetic moment value obtained for **2** is 1.85 μ_B (spin-only $\mu_B = 1.73$ μ_B). Complex **3** shows a magnetic moment of 4.25 μ_B (spin-only $\mu_B = 3.87$ μ_B).[23] These results show that in these dinuclear heterobimetallic derivatives the electronic interaction between the metal ions is minimal, at least, at room temperature. It should be mentioned, however, that low-temperature magnetic measurements by Ainscough et al. on [(MeL)($CuCl_2$)$_2$] revealed an increase in molar magnetic susceptibility as the temperature approached 0 K.[12b] This was fitted to $g = 2.10$ and a $2J$ value of -1 cm^{-1}. The weak magnetic interaction that occurs even at very low temperature has been attributed to poor orbital overlap and is in agreement with the nature of the bonding in cyclophosphazene rings.[12b] The ineffectiveness of the cyclophosphazene ligand in establishing electronic communication between two metal centers has also been noted in other instances.[12b] In view of this, the room-temperature magnetic data of **1** is consistent with noninteracting or weakly interacting metal ions. The room-temperature magnetic moment value of compound **5** is 5.61 μ_B. This value is consistent with a formal oxidation state of +2 for all the three metal ions in **5** (spin-only $\mu_B = 5.92$ μ_B).

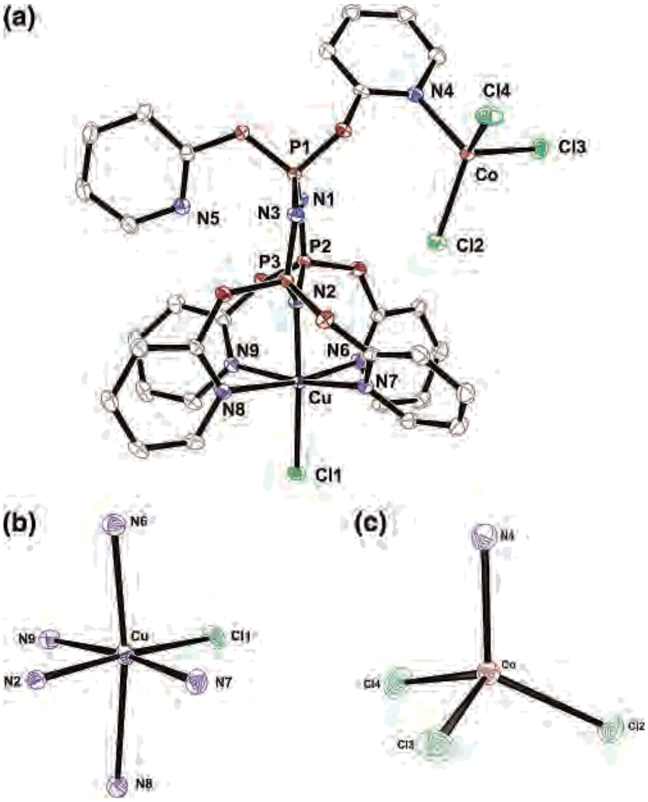


Figure 1. (a) ORTEP diagram of **1**. Hydrogen atoms have been omitted for clarity. (b) The distorted octahedral coordination environment around theCu(II) ion in **1**. (c) The distorted tetrahedral coordination environment around the Co(II) ion in **1**.

^{31}P NMR of complexes **1**–**3** and **5** were affected by the paramagnetic nature of the metal ions. The dinuclear zinc complex **4** shows a singlet at 5.09 ppm which is slightly upfield shifted with respect to the free ligand (6.37 ppm). Although an AB_2 or AX_2 type of spectrum is anticipated for **4** in view of its molecular structure as determined in the solid-state (vide infra), only a single resonance is seen, because of either the isochronous chemical shift or the $\eta^3 - \eta^2$ fluxional behavior. Do and co-workers have reported earlier a similar fluxional behavior for ($N_3P_3$3,5-Me_2Pz)$_6$.($ZnCl_2$)$_2$.[7b,7c] The spectral behavior of **4** does not change up to −40 °C as noted by the invariance of the chemical shift as well as the appearance of the spectrum. Infrared spectra of complexes **1**–**5** reveal that the ν(P=N) seen for the free ligand at 1182 and 1222 cm^{-1} is altered upon complexation. New peaks at 1302 (**1**), 1303 (**2**), 1305 (**3**), 1301 (**4**), and 1295 cm^{-1} (**5**) are seen, while the peak at 1222 cm^{-1} is split indicating the involvement of the cyclophosphazene ring nitrogen atom in coordination to the metal ion. This feature is similar to that observed previously in the case of pyrazolyl cyclophosphazenes as well as pyridyloxy cyclophosphazenes.[2,10,12b] The involvement of the cylcophosphazene ring nitrogen coordination is corroborated the X-ray crystal structure analysis.

X-ray Crystal Structures of 1–**3.** Compounds **1**–**3** are isostructural, and they crystallize as isomorphous crystals with three molecules of dichloromethane and one molecule of water as solvents of crystallization (space group $P\bar{1}$). The ORTEP diagram of **1** is given in Figure 1a. The molecular structures of **2** and **3** are given in the Supporting Information.

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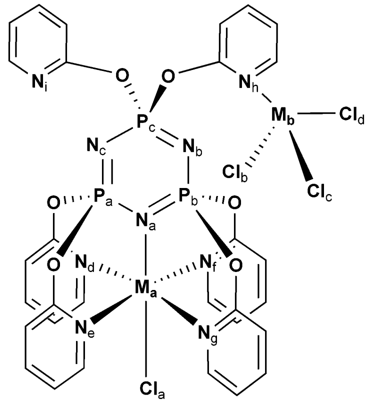
The molecular structures of the dinuclear heterobimetallic compounds, **1**−**3**, reveal that the two metal ions possess different coordination geometries. One of the metals (M_a, see Scheme 1) has a coordination number of six (5N, 1Cl) and is present in a distorted rhombic octahedral geometry, while the other metal (M_b) is tetracoordinate (1N, 3Cl) and is present in a distorted tetrahedral geometry (Figure 1b and c). The nitrogen coordination environment around M_a can be described as η^5-gem-N_5 with four of the five coordinating nitrogen atoms derived from the geminally substituted pyridyloxy groups: the fifth donor nitrogen atom is from the cyclophosphazene ring. The coordination environment of M_b consists of one pyridyloxy nitrogen and three chloride ligands. Thus, in the formation of heterobimetallic derivatives **1**−**3**, the ligand **L** utilizes six of the possible nine coordination sites. It is interesting to compare this coordination behavior with that observed for pyrazolyl cyclotriphosphazenes and cyclophosphazenes hydrazides. While in the former, the coordination response is predominantly η^3-nongem-N_3[10] (with only one example of a η^5-gem-N_5[7a] and another example of an η^2-gem-N_2),[7b] in the latter, 2:1 (L/M) complexes are formed with an η^3-nongem-N_3 coordination mode.[3g] Even with **L**, the η^3-nongem-N_3[12b] mode has been observed earlier and in the present instance in **4** (vide infra). The η^5-gem-N_5 coordination mode appears to be solicited from **L** only when the metal ion involved has one anionic ligand (Cl^-) attached to it.

The metric parameters for compounds **1**−**3** are summarized in Table 3. The cyclophosphazene ring is nearly planar in all three complexes suggesting that the inorganic ring does not have to undergo structural rearrangement upon coordination. This is in contrast to the situation found in the metal complexes obtained from the pyrazolyl cyclophosphazenes.[10] Clearly, the oxygen spacer atom separating the coordinating unit in the present instance relieves steric strain and accounts for the planarity of the cyclophosphazene ring in complexes **1**−**3**. The bond parameters for the phosphazene ring in **1**−**3** indicate that there is significant elongation in the P−N bonds (P_a−N_a and P_b−N_a) that flank the coordinating ring nitrogen atom. This feature which has been observed earlier upon protonation or metalation involving the ring nitrogen atoms[1f,2b,10a,24,25] (entries 1 and 2, Table 3) is consistent with current bonding models of cyclophosphazene.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**−**3** and Related Compounds



		1	**2**	**3**	[LCuCl] PF_6[12b]	[$L_2Cu_3Cl_4$] [Cu_2Cl_6][12a]
1	P_a−N_a	1.597(2)	1.602(3)	1.589(3)	1.597(3)	1.603(2)
2	P_b−N_a	1.604(2)	1.601(3)	1.594(3)	1.601(3)	1.597(2)
3	P_b−N_b	1.562(2)	1.562(3)	1.561(3)	1.566(3)	1.565(3)
4	P_c−N_b	1.582(2)	1.581(3)	1.583(3)	1.581(3)	1.584(3)
5	P_c−N_c	1.582(2)	1.580(3)	1.579(3)	1.589(3)	1.584(3)
6	P_a−N_c	1.564(2)	1.566(3)	1.566(3)	1.550(3)	1.567(2)
7	M_a−N_a	1.988(2)	1.982(3)	2.048(3)	1.993(3)	1.988(2)
8	M_a−N_e	2.089(2)	2.085(3)	2.179(3)	2.140(3)	2.090(3)
9	M_a−N_f	2.116(2)	2.111(3)	2.212(3)	2.214(3)	2.093(2)
10	M_a−N_d	2.603	2.615	2.433(3)	2.483(3)	2.559(3)
11	M_a−N_g	2.413(2)	2.423(3)	2.297(3)	2.467(3)	2.509(3)
12	M_a−Cl_a	2.2434(7)	2.2375(9)	2.3102(9)	2.2281(9)	2.2492(9)
13	M_b−N_h	2.082(2)	2.111(3)	2.101(3)		
14	M_b−Cl_b	2.2453(8)	2.2331(9)	2.2369(9)		
15	M_b−Cl_c	2.2564(8)	2.2559(9)	2.2544(10)		
16	M_b−Cl_d	2.2621(8)	2.2564(9)	2.2558(9)		
17	M_a− M_b	6.895	6.902	6.958		
18	P_a−N_a−P_b	123.38(14)	123.33(17)	123.37(17)		
19	P_b−N_b−P_c	121.53(14)	120.52(17)	120.51(17)		
20	P_a−N_c−P_c	120.44(15)	121.61(17)	121.36(18)		
21	N_c−P_a−N_a	116.02(12)	116.35(15)	116.79(15)		
22	N_a−P_b−N_b	116.34(12)	115.81(14)	116.55(15)		
23	N_b−P_c−N_c	119.38(12)	119.32(14)	119.40(15)		
24	N_a−M_a−Cl_a	175.74(7)	175.96(8)	176.49(8)		
25	N_d−M_a−N_g	171.79	171.67	171.80(10)		
26	N_e−M_a−N_f	169.98(9)	170.15(11)	167.26(11)		
27	N_h−M_b−Cl_b	118.49(7)	116.85(8)	116.02(8)		
28	N_h−M_b−Cl_c	103.92(7)	100.38(8)	102.58(8)		
29	N_h−M_b−Cl_d	100.73(7)	103.16(8)	101.15(8)		

The metric parameters around the metal centers in **1**−**3** are also summarized in Table 3. The coordination geometry around M_a can be thought of as comprising a basal plane (N_e, N_a, N_f, and Cl_a) and two axial ligands (N_d and N_g). The M_a−N axial distances (the nitrogens derived from nongeminal pyridyloxy substituents) are longer than those observed in the basal plane (Table 3, entries 7−2). This feature is accentuated in the copper-containing complexes, **1** and **2** (Table 3, entries 7−2), and is consistent with literature precedents (Table 3, entries 7−12). In all the cases, the M−N_a distance (involving the cyclophosphazenes ring nitrogen) is the shortest. A further point of interest is that M_a is coplanar with the cyclophosphazenes ring [displacement of M_a from the mean cyclophosphazene plane = 0.065 (**1**), 0.062 (**2**), and 0.062 Å (**3**)]. The M_b−N_h distances are fairly short and range from 2.082 to 2.111 Å. The M−Cl distances observed (M_a−Cl and M_b−Cl distance) are comparable (Table 3 entries 12 and 14−16).

The molecular structure of **4** is different from those observed for **1**−**3.** The ORTEP diagram for **4** is given in Figure 2. The molecular structure of **4** reveals that ligand **L** bridges two zinc chloride units. The two zinc ions present have two different coordination geometries. Thus, Zn(1) is tetracoordinate (2N, 2Cl; η^2-gem-N_2), while Zn(2) is five-coordinate (3N, 2Cl; η^3-nongem-N_3). These coordination modes lead to the generation of three new cyclic rings: an eight-membered ring (Zn1−N4−C−O1−P1−O2−C−N5) and two six-membered rings (Zn2−N8−C−O5−P2−N3, Zn2−N6−C−O3−P3−N3). The coordination response of **L** toward the two zinc ions is similar to that found in dinuclear zinc complexes obtained from $N_3P_3(3,5\text{-}Me_2\text{-}Pz)_6$.[7b,7c] The coordination environment Zn1 is distorted tetrahedral, while a distorted trigonal bipyramidal environ-

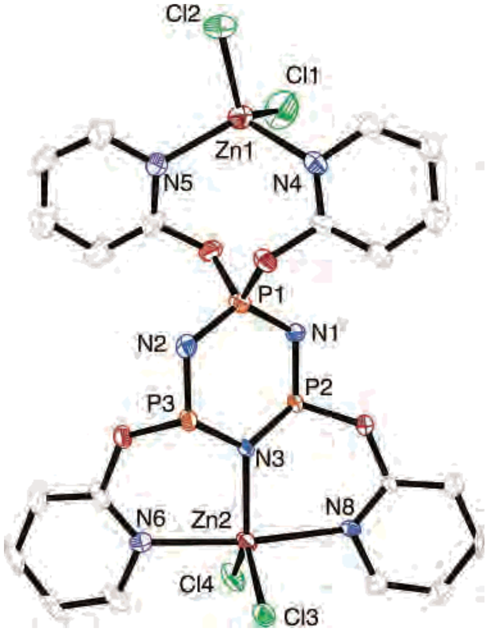


Figure 2. ORTEP diagram of **4**. Hydrogen atoms and the two uncoordinated nongem pyridyloxy units have been omitted for clarity.

ment is seen around Zn2. The axial positions in the TBP geometry around Zn2 are occupied by the nongeminal pyridyloxy nitrogen atoms N8 and N6 (N8−Zn2−N6 = 173.1°). The equatorial positions are spanned by the two chloride ligands and the cyclotriphosphazene ring nitrogen atom (N3). The structural index τ which defines the extent of deviation from trigonal bipyramidal to square pyramidal geometry ($\tau = 1$ for perfect trigonal bipyramidal; $\tau = 0$ for perfect square based pyramid)[26] is 0.77 indicating only small deviation from the regular TBP geometry. The Zn2−N distances reveal that the distance involving the cyclophosphazene ring (Zn2−N3 = 2.080(5) Å) is shorter than those involving the pyridyloxy nitrogen atoms (Zn2−N6 = 2.276(6) Å, Zn2−N8 = 2.319(5) Å) consistent with the situation for compounds **1**−**3**. Similarly, Zn1−N distances (Zn1−N5 = 2.046(6) Å, Zn1−N4 = 2.096(6) Å) are quite short. Even in the case of **4**, the cyclophosphazene ring is planar and does not undergo any distortion. The metric parameters observed in the cyclophosphazene ring for **4** are comparable to those found in **1**−**3** (Table 3).

Compound **5** crystallizes with three molecules of dichloromethane and one molecule of water (space group *Fddd*). The cationic part of complex **5** is as shown in Figure 3a. The molecular structure of **5** contains two copper-metalated cyclophosphazene units [(CuCl)$N_3P_3(OC_5H_4N)_5(O)$], which are bridged by a central cobalt(II) ion. At this stage we have been unable to decipher the precise mechanistic pathway of the P−O bond scission. It is, however, clear that the P−O bond cleavage occurs only after the addition of cobalt nitrate.

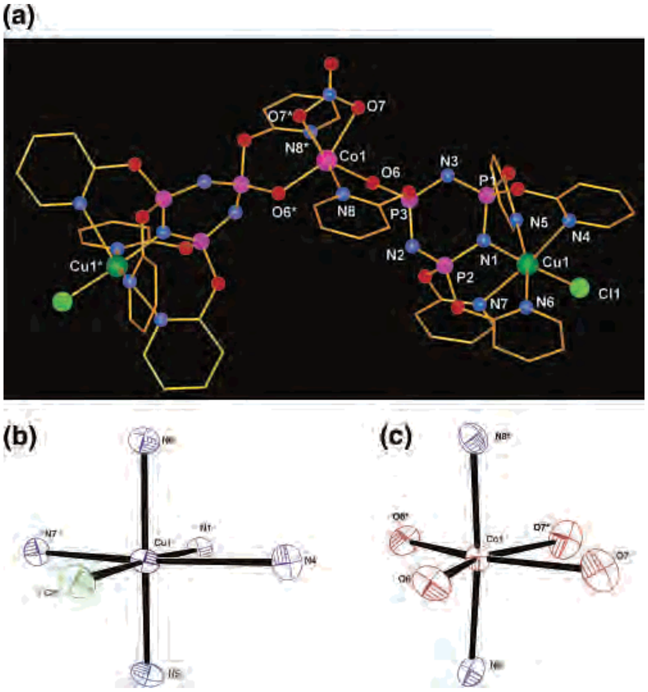


Figure 3. (a) DIAMOND picture of cationic part of the complex **5**. Hydrogen atoms have been omitted for clarity. (**b)** The distorted octahedral coordination environment around the Cu(II) ion in **5**. (c) The distorted octahedral coordination environment around the Co(II) ion in **5**.

Compound **5** is structurally similar to a trinuclear derivative [$L_2Cu_3Cl_4$][Cu_2Cl_6] reported by Ainscough and co-workers.[12a] However, the latter is a homometallic derivative in contrast to the heterometallic nature of **5**. Furthermore, the ligand is intact in contrast to the P−O bond cleavage observed during the formation of **5**. The coordination environment (5N, 1Cl) and the coordination geometry (distorted rhombic octahedral geometry) around the two copper centers in the fragment [(CuCl)$N_3P_3(OC_5H_4N)_5(O)$] are similar to that found in the dinuclear heterobimetallic compounds **1** and **2**. However, in contrast to the that in **5**, the copper atom is displaced from the mean plane of the cylcophospahzene ring by 0.22 Å. The bridging cobalt center is hexacoordinate (2N, 4O). The two nitrogen atoms are derived from the pyridyloxy substituents of the two cyclophosphazene ligands. Two of the coordinating oxygen atoms are from the in situ-generated P−O units. The remaining two oxygen atoms belong to the chelating nitrate ligand. Some important metric parameters for **5** are summarized in Table 5. The distances around copper are very similar to those found for **1** and **2** and involve two short (av 2.107(3) Å) and two long (av 2.510(3) Å) Cu−N bond distances. Two types of Co−O distances are seen: the Co−O6 distance (1.998(3) Å) is slightly shorter than the Co−O7 (2.205(4) Å) distance. The Co−N distance (2.135 (3) Å) is comparable to that found in **3**. The distance involving the hydrolyzed P−O unit, P3−O6 (1.494(3) Å), is considerably shorter than the other P−O distances found in **5**, as well as those in compounds **1**−**4.** The short length of the P−O distance found for **5** is comparable to the P=O distance observed in many compounds. For example, in PhP(O)$(OH)_2$, the comparable distance is 1.506(5) Å,[27a] and in P(O)[N(Me)-NH_2]$_3$, it is 1.4853(10) Å.[27b] Significant elongation of the

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

1	Zn(1)−N(5)	2.046(6)
2	Zn(1)−N(4)	2.096(6)
3	Zn(1)−Cl(2)	2.212(2)
4	Zn(1)−Cl(1)	2.225(2)
5	Zn(2)−N(3)	2.080(5)
6	Zn(2)−N(6)	2.276(6)
7	Zn(2)−N(8)	2.319(5)
8	Zn(2)−Cl(4)	2.2432(19)
9	Zn(2)−Cl(3)	2.2496(19)
10	P(1)−N(1)	1.562(5)
11	P(1)−N(2)	1.559(5)
12	P(2)−N(1)	1.563(5)
13	P(2)−N(3)	1.612(5)
14	P(3)−N(2)	1.561(6)
15	P(3)−N(3)	1.609(5)
16	Zn(1)−Zn(2)	9.110
17	N(5)−Zn(1)−Cl(2)	105.14(18)
18	N(4)−Zn(1)−Cl(2)	105.69(17)
19	N(5)−Zn(1)−Cl(1)	110.36(18)
20	N(4)−Zn(1)−Cl(1)	101.13(17)
21	N(5)−Zn(1)−N(4)	115.9(2)
22	Cl(2)−Zn(1)−Cl(1)	119.09(10)
23	N(3)−Zn(2)−Cl(4)	126.56(15)
24	N(3)−Zn(2)−Cl(3)	116.23(15)
25	Cl(4)−Zn(2)−Cl(3)	117.21(8)
26	N(3)−Zn(2)−N(6)	87.45(19)
27	Cl(4)−Zn(2)−N(6)	91.13(14)
28	Cl(3)−Zn(2)−N(6)	92.31(14)
29	N(3)−Zn(2)−N(8)	86.41(18)
30	Cl(4)−Zn(2)−N(8)	90.08(14)
31	Cl(3)−Zn(2)−N(8)	93.14(13)
32	N(6)−Zn(2)−N(8)	173.14(19)
33	N(2)−P(1)−N(1)	119.3(3)
34	N(1)−P(2)−N(3)	116.7(3)
35	N(2)−P(3)−N(3)	117.6(3)
36	P(1)−N(1)−P(2)	122.0(3)
37	P(1)−N(2)−P(3)	122.1(3)
38	P(3)−N(3)−P(2)	120.8(3)

P−N distances flanking the sites of coordination is observed in **5** (Table 5). This is consistent with the observations in **1**−**4**, as well as in other metalated cyclophosphazenes.

Conclusion

The multisite coordination ligand, **L**, is quite versatile for the assembly of hetero- and homobimetallic derivatives. The architecture of the ligand involving the spacer oxygen atoms which separate the coordinating pyridyloxy substituents from the cyclophosphazenes ring allows a *strain-free* coordination response from the ligand. An interesting corollary of the latter feature is the ease with which the coordination response is modulated depending on the metal environment. Thus an MCl_2 unit is bound by a η^3-nongem-N_3 mode or by a η^2-gem-N_2 mode, while an MCl_3 unit is bound by a η^1-N_1 mode. On the other hand, an MCl unit is bound by a η^5- gem-N_5 mode. An unusual P−O bond cleavage is observed in the reaction of **L** with $CuCl_2$, followed by the addition of $Co(NO_3)_2 \cdot 6H_2O$. Although the mechanistic details of this reaction still elude us, we have been able to isolate a novel trinuclear heterobimetallic (Cu_2Co) derivative. In this compound the CuCl fragment is bound to the cyclophosphazene ligand in a η^5- gem-N_5 mode, while the $Co(O_2NO)$ fragment is bound by two cyclophosphazenes each in a η^2-gem-N,O mode. The above versatile and diverse coordination behavior of **L** is a testimony to the efficacy of utilizing cyclophosphazenes as scaffolds for the construction of new multisite coordination ligands.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

1	Cu(1)−N(1)	1.967(3)
2	Cu(1)−N(4)	2.565
3	Cu(1)−N(5)	2.108(3)
4	Cu(1)−N(6)	2.095(3)
5	Cu(1)−N(7)	2.456(3)
6	Cu(1)−Cl(1)	2.2267(10)
7	Co(1)−N(8	2.135(3)
8	Co(1)−O(7)	2.205(4)
9	Co(1)−O(6)	1.998(3)
10	P(1)−N(3)	1.552(3)
11	P(1)−N(1)	1.604(3)
12	P(2)−N(2)	1.547(3)
13	P(2)−N(1)	1.599(3)
14	P(3)−N(2)	1.609(3)
15	P(3)−N(3)	1.604(3)
16	P(1)−O(1)	1.573(3)
17	P(1)−O(2)	1.594(3)
18	P(2)−O(3)	1.581(3)
19	P(2)−O(4)	1.592(3)
20	P(3)−O(5)	1.619
21	P(3)−O(6)	1.494(3)
22	Cu(1)−Cu(1*)	14.070
23	Cu(1)−Co(1)	8.167
24	N(1)−Cu(1)−Cl(1)	176.16(10)
25	N(6)−Cu(1)−N(5)	167.78(12)
26	N(4)−Cu(1)−N(7)	171.07
27	O(6)−Co(1)−N(8)	87.97(12)
28	O(6)−Co(1)−O(7)	94.53(12
29	N(8)−Co(1)−O(7)	90.74(13)
30	N(3)−P(1)−N(1)	115.64(17)
31	N(2)−P(2)−N(1)	116.26(17)
32	N(3)−P(3)−N(2)	114.95(17)
33	P(2)−N(1)−P(1)	122.11(18)
34	P(2)−N(2)−P(3)	122.6(2)
35	P(1)−N(3)−P(3)	123.1(2)

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Supporting Information Available: Figures S1 and S2 showing ORTEP diagrams of compounds **2** and **3**, Figures S3 and S4 showing EPR spectra of compounds **1** and **2** at 120 K, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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