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Cyclotriphosphazene Hydrazides as Efficient Multisite Coordination Ligands. η^3-*fac*-*non*-*geminal*-N_3 Coordination of *spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$ (L) in L_2CoCl_3 and $L_2M(NO_3)_2$ (M = Ni, Zn, Cd)

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The cyclophosphazene tetrahydrazide *spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$ (L) functions as a multisite coordination ligand and affords $L_2CoCl_3\cdot 2CH_3OH$ (**4**), $L_2Ni(NO_3)_2\cdot 2CHCl_3\cdot 2.5H_2O$ (**5**), $L_2Zn(NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$ (**6**), and $L_2Cd(NO_3)_2$ (**7**). Each of the cyclophosphazene ligands that is involved in coordination to the metal functions as a *non*-*geminal*-N_3 donor coordinating through one ring nitrogen atom and two *non*-*geminal*-NH_2 nitrogen atoms. The coordination geometry around the metal ion in **4**–**6** is approximately octahedral while it is severely distorted in the case of **7**.

Introduction

There is considerable contemporary interest in the use of cyclophosphazene-based ligand systems.[1] This is primarily due to the fact that it is possible to use the cyclophosphazene rings as scaffolds for the design and construction of a variety of ligands each of which can provide unique steric and electronic environments for transition metal coordination.[2] Additionally, the interaction of cyclophosphazene-based multisite coordination ligands with transition metal ions can lead to metal-rich assemblies possessing interesting catalytic or magnetic properties.[3] Also, the unique relationship between cyclo- and polyphosphazenes allows the small molecule chemistry to be readily translated to the polymeric analogues.[4] Thus, recently we have demonstrated the varied coordination capability of pyrazolyl cyclophosphazenes[5] and have also been able to show the practical utility of their polymeric analogues in catalytic applications involving phosphate ester hydrolysis.[6] Other groups have also been able to use cyclophosphazene-based ligands for achieving novel main-group,[7] transition,[8] and lanthanide[3d] metal assemblies. In view of the versatility of the hydrazine motif[9] as a ligand

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Table 1. Crystal and Structure Refinement Data for Compounds **4**−**7**

params	**4**	**5**	**6**	**7**
empirical formula	$C_{34}H_{64}Cl_3CoN_{22}O_6P_6$	$C_{34}H_{63}Cl_6N_{24}NiO_{12.50}P_6$	$C_{36}H_{66}N_{26}O_{12}P_6Zn$	$C_{32}H_{56}CdN_{24}O_{10}P_6$
fw	1228.17	1465.31	1306.34	1235.23
temp (K)	213(2)	150(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1$	$P2_1/c$	$P2_1/c$	$C222_1$
unit cell dimens (Å, deg)	$a = 8.1714(12)$	$a = 15.2295(11)$	$a = 16.3310(9)$	$a = 9.9584(5)$
	$b = 21.337(3)$	$b = 13.1274(10)$	$b = 15.5539(9)$	$b = 17.1445(9)$
	$c = 16.404(2)$	$c = 16.3455(12)$	$c = 12.7101(7)$	$c = 31.4379(16)$
	$\beta = 94.920(17)$	$\beta = 103.720(10)$	$\beta = 108.546(10)$	
V (Å^3), Z	2849.7(7), 2	3174.6(4), 2	3060.8(3), 2	5367.4(5), 4
D(calcd) (Mg/m^3)	1.431	1.533	1.417	1.529
abs coeff (mm^{-1})	0.671	0.782	0.632	0.659
F(000)	1276	1510	1360	2536
cryst size	0.4 × 0.4 × 0.2	0.4 × 0.3 × 0.2	0.7 × 0.6 × 0.5	0.5 × 0.6 × 0.6
θ range for data collcn (deg)	2.28−24.20	2.01−24.11	1.32−28.32	2.37−28.28
limiting indices	$-9 \le h \le 9$	$-17 \le h \le 15$	$-10 \le h \le 21$	$-13 \le h \le 12$
	$-24 \le k \le 24$	$-12 \le k \le 15$	$-20 \le k \le 19$	$-21 \le k \le 22$
	$-18 \le l \le 18$	$-18 \le l \le 18$	$-16 \le l \le 15$	$-41 \le l \le 33$
reflcns collcd	18 118	15 055	18 759	16 801
indpdt reflcns	8566 ($R_{int} = 0.0384$)	5035 ($R_{int} = 0.0423$)	7022 ($R_{int} = 0.0158$)	6171 ($R_{int} = 0.0261$)
absolute struct param	0.13(5)			−0.05(2)
max and min transm	-		1.000 and 0.885	0.976 and 0.793
data/restraints/params	8566/25/707	5035/71/405	7022/66/519	6171/73/382
goodness-of-fit on F^2	1.051	1.021	1.054	1.072
final R indices [$I > 2\sigma(I)$]	R1 = 0.0398,	R1 = 0.0632,	R1 = 0.0387,	R1 = 0.0430,
	wR2 = 0.1038	wR2 = 0.1684	wR2 = 0.1161	wR2 = 0.1151
R indices (all data)	R1 = 0.0451,	R1 = 0.0727,	R1 = 0.0417,	R1 = 0.0473,
	wR2 = 0.1077	wR2 = 0.1767	wR2 = 0.1179	wR2 = 0.1181
largest diff peak and hole (e Å^{-3})	0.433 and −0.403	1.000 and −1.076	0.874 and −0.433	1.186 and −0.413

and also in view of our recent interest in cyclophosphazene hydrazones,[10] we have been interested in using cyclophosphazene hydrazides with multiple hydrazine arms as multisite coordination ligands for interacting with transition metal ions. Accordingly we report the first examples of transition metal assemblies built from the cyclophosphazene hydrazide *spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$ (**3**; L). In the following account, we describe the synthesis and structural characterization of $L_2{\cdot}CoCl_3$ (**4**) and $L_2{\cdot}M(NO_3)_2$ [M = Ni(II) (**5**); M = Zn(II) (**6**); M = Cd(II) (**7**)]. The compounds **4**−**7** have been isolated as their cationic complexes.

Experimental Section

General Methods. Solvents and other general reagents used in this work were purified according to standard procedures. 2,2′-Dihydroxybiphenyl (Fluka) was used as received. $N_3P_3Cl_6$ (Aldrich, Milwaukee, WI) was recrystallized from *n*-hexane before use. *N*-Methylhydrazine was obtained as a gift from the Vikram Sarabhai Space Research Centre, Thiruvananthapuram, India, and used as received. $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, and $CoCl_2{\cdot}6H_2O$ were obtained from S.D. Fine Chemicals, Mumbai, India. *spiro*-$N_3P_3(O_2C_{12}H_8)Cl_4$ was prepared according to the procedure reported in the literature.[11]

Instrumentation. ^1H and $^{31}P\{^1H\}$ 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 (^1H) and external 85% H_3PO_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 FT IR spectrophotometer operating from 400 to 4000 cm^{-1}. Electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV−vis spectrometer and on a Shimadzu UV-160 spectrometer using DMF as the solvent. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model.

X-ray Crystallography. The crystal data for **4**−**7** are given in Table 1. In the case of **4** suitable crystals were obtained by slow evaporation of its solution in a mixture of methanol and dichloromethane (70:30). Suitable crystals of **5** were obtained by slow evaporation of a solution in methanol and chloroform (70:30) while those of **6** and **7** were obtained by slow evaporation of acetonitrile solutions. The crystal data for compound **4** was collected on a Stoe IPDS diffractometer while those for the compounds **5**−**7** were collected on a Bruker AXS Smart Apex diffractometer. Crystal structures were refined against F^2 using all data by a full-matrix least-squares algorithm (SHELX).[12] Non-hydrogen atoms were refined with anisotropic displacement parameters if not stated otherwise. H-positions in **4**, **5**, and **7** were set geometrically, except for $-NH_2$ groups of hydrazine units, which were located from difference maps, and their positions were refined using distance

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restraints. All H-positions in **6** were refined freely. In the structures of **5**−**7** the nitrate anions were severely disordered. The $CHCl_3$ molecule and the nitrate ion in **5** are disordered. They were split on two positions and refined isotropically using similar distance and similar U restraints. The occupancy factors for the major domains of the $CHCl_3$ and nitrate sites refined to 0.56602 and 0.526, respectively. Residual electron density within the channels located near the crystallographic inversion center was assigned to a cluster of 2.5 disordered water molecules, which were refined isotropically as O-atoms without H-positions. The oxygen positions of NO_3^- ion in **6** are disordered. They were split on two positions and were refined anisotropically using similar distance and similar *U* restraints. The occupancy factor for the major domain refined to 0.773. There is one noncoordinated water molecule in the asymmetric unit of **6**. It is in hydrogen-bonding distance to two NH_2 groups of one ligand, the acetonitrile molecule, and both domains of the disordered nitrate ion. H-atoms could not be located from the difference map and, thus, were omitted from the refinement. The nitrate ions in **7** are disordered around crystallographic 2-fold axes. N and O atoms of the ions were refined anisotropically using similar distance and similar *U* restraints and occupancy factors of 0.5.

Synthesis

***spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$ (3).** *spiro*-$N_3P_3(O_2C_{12}H_8)Cl_4$ (2.11 g, 4.58 mmol) dissolved in dry chloroform (50 mL) was added dropwise for about 0.5 h to a solution of $HN(Me)NH_2$ (1.69 g, 36.60 mmol) in chloroform (40 mL) at 0 °C. The reaction mixture was stirred for 24 h at 25 °C, and the $HN(Me)NH_2$·HCl that was formed in the reaction was filtered. Removal of solvent from the filtrate afforded a solid product. This was dissolved in hot acetonitrile (60 mL) and allowed to come to 25 °C to obtain a white crystalline solid. Yield: 2.04 g (89.5%). Mp: 208−210 °C. ^{1}H NMR ($CDCl_3$, ppm): 2.84 (d, 12H, P(N−CH_3), $^3J(^1H-^{31}P) = 10.9$ Hz), 3.46 (s (broad), 8H, −NH_2), 7.14 (d, 2H, aromatic, ^3J(H−H) = 7.3 Hz), 7.24 (dd, 2H, aromatic, ^3J(H−H) = 7.3 Hz), 7.34 (dd, 2H, aromatic, ^3J(H−H) = 7.3 Hz), 7.47 (d, 2H, aromatic, ^3J(H−H) = 7.3 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): 27.2 (t, *P*($O_2C_{12}H_8$)), 29.9 (d, *P*(N(Me)NH_2), ^2J(P−N−P) = 53.4 Hz. FAB-MS: *m*/*z* 499 (M^+). IR (KBr, cm^{-1}): 3431 (b), 3320 (m), 2942 (m), 1611 (m), 1442 (s), 1215 (s), 1173 (s), 1098 (m), 1018 (m), 956 (m), 865 (s), 741 (s). Anal. Calcd for $C_{16}H_{28}N_{11}P_3O_2$: C,38.48; H, 5.65; N, 30.85; Found: C, 37.83; H, 5.83; N, 29.67.

Synthesis of the Metal Complexes 4−7. The general procedure of preparation of the metal complexes is as follows. To a solution of the ligand **3** (0.200 g, 0.40 mmol) in acetonitrile (30 mL) was added a solution of $CoCl_2$·$6H_2O$ (0.20 mmol) in methanol (20 mL) or $M(NO_3)_2$·xH_2O (0.20 mmol) in acetonitrile (20 mL). After being stirred for 3 h at room temperature, the reaction mixture was concentrated to a volume of 5 mL. To this solution, 20 mL of diethyl ether was added upon which a solid was precipitated. This was filtered out, dried, and purified by crystallization to afford L_2CoCl_3·$2CH_3OH$ (**4**), $L_2Ni(NO_3)_2$·$2CHCl_3$·$2.5H_2O$ (**5**), $L_2Zn(NO_3)_2$·$2CH_3CN$·$2H_2O$ (**6**), and $L_2Cd(NO_3)_2$ (**7**). The characterization data for these compounds are given below.

L_2CoCl_3·$2CH_3OH$ (4). Yield: 0.18 g (78.3%). Mp: 220 °C (dec). ^{1}H NMR (DMSO-d_6, ppm): 3.08 (d, 12H, (N−CH_3), $^3J(^1H-^{31}P) = 10.1$ Hz), 7.13 (d, 2H, aromatic, ^3J(H−H) = 7.9 Hz), 7.39 (dd, 2H, aromatic, ^3J(H−H) = 7.3, 7.9 Hz), 7.46 (dd, 2H, aromatic, ^3J(H−H) = 7.3,7.6 Hz), 7.59 (d, 2H, aromatic, ^3J(H−H) = 7.6 Hz). ^{31}P NMR (DMSO-d_6, ppm): 19.7 (t, *P*($O_2C_{12}H_8$)), 35.4 (d, *P*[(N(Me)NH_2)$_2$), ^2J(P−N−P) = 63.1 Hz). IR (KBr,cm^{-1}): 3404 (b), 3247 (m), 2940 (m), 1616 (s), 1473 (m), 1441 (s), 1278 (m), 1229 (m), 1182 (m), 1093 (m), 971 (m), 845 (m), 780 (s). Anal. Calcd for $C_{34}H_{64}Cl_3N_{22}O_6P_6Co$: C, 33.25; H, 5.25; N, 25.09. Found: C, 33.06; H, 4.71; N, 25.11.

$L_2Ni(NO_3)_2$·$2CHCl_3$·$2.5H_2O$ (5). Yield: 0.18 g (75.0%). Mp: 205 °C (d). IR (KBr, cm^{-1}): 3411 (b), 3227 (m), 2939 (m), 1624 (s), 1472 (m), 1435 (m), 1382 (s), 1267 (m), 1224 (m), 1178 (m), 1089 (s), 965 (m), 776 (s). UV−vis {DMF [λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})]}: 970 (8.5), 595 (7.4), 353 (20.6), 279 (261.9). Solution magnetic moment: $\mu_B = 2.92$ BM (after applying diamagnetic corrections). Anal. Calcd for $C_{68}H_{126}Cl_{12}N_{48}O_{25}P_{12}Ni_2$: C, 27.87; H, 4.33; N, 22.94. Found: C, 27.11; H, 4.55.; N, 22.47.

$L_2Zn(NO_3)_2$·$2CH_3CN$·$2H_2O$ (6). Yield: 0.20 g (83.3%), Mp: 250 °C (d). ^{1}H NMR (DMSO-d_6, ppm): 2.83 (d, 12H, (N−CH_3), $^3J(^1H-^{31}P) = 10.5$ Hz), 7.23 (d, 2H, aromatic, ^3J(H−H) = 7.8 Hz), 7.44 (dd, 2H, aromatic, ^3J(H−H) = 7.6, 7.3 Hz), 7.54 (dd, 2H, aromatic, ^3J(H−H) = 7.6 Hz), 7.69 (d, 2H, aromatic, ^3J(H−H) = 7.6 Hz). ^{31}P NMR (DMSO-d_6, ppm): 24.0 (t, *P*($O_2C_{12}H_8$)), 26.7 (d, *P*[(N(Me)NH_2)$_2$), ^2J(P−N−P) = 61.4 Hz). IR (KBr) (ν/cm^{-1}): 3206 (b), 3124 (m), 2936 (w), 1614 (m), 1438 (w), 1380 (s), 1268 (m), 1223 (m), 1182 (s), 1064 (m), 974 (m), 776 (s). Anal. Calcd for $C_{32}H_{66}N_{26}O_{12}P_6Zn$: C, 33.10; H, 5.09; N, 27.88. Found: C, 32.81; H, 4.64.; N, 27.37.

$L_2Cd(NO_3)_2$ (7). Yield: 0.19 g (76.0%). Mp: 240 °C (d). ^{1}H NMR (DMSO-d_6, ppm): 2.84 (d, 12H, (N−CH_3), $^3J(^1H-^{31}P) = 10.0$ Hz), 7.20 (d, 2H, aromatic, ^3J(H−H) = 7.8 Hz), 7.45 (dd, 2H, aromatic, ^3J(H−H) = 7.8, 7.3 Hz), 7.54 (dd, 2H, aromatic, ^3J(H−H) = 7.6, 7.3 Hz), 7.69 (d, 2H, aromatic, ^3J(H−H) = 7.3 Hz). ^{31}P NMR (DMSO-d_6, ppm): 24.6 (t, *P*($O_2C_{12}H_8$)), 26.4 (d, *P*[(N(Me)NH_2)$_2$), ^2J(P−N−P) = 58.2 Hz). IR (KBr, cm^{-1}): 3464 (b), 3255 (m), 2934 (m), 1612 (m), 1441 (m), 1378 (s), 1270 (m), 1226 (m), 1182 (s), 1096 (m), 973 (m), 778 (s). Anal. Calcd for $C_{32}H_{56}N_{24}O_{10}P_6Cd$: C, 31.12; H, 4.57; N, 27.22. Found: C, 31.04; H, 4.24; N, 27.51.

Results and Discussion

Synthetic Aspects. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), with its reactive periphery of six P−Cl bonds is an ideal target for elaboration into a multisite coordination ligand. To obtain amenable ligands which are likely to yield soluble molecular complexes rather than intractable polymeric species we have chosen to block one of the phosphorus sites by a noninteracting group. This is accomplished by the known reaction of **1** with 2,2′-biphenol in acetone in the presence of K_2CO_3 to afford *spiro*-$N_3P_3Cl_4[O_2C_{12}H_8]$[11] (**2**), which now contains only four P−Cl bonds. Reaction of **2** with *N*-methylhydrazine results in a regiospecific substitution at its N−CH_3 end to afford the tetrahydrazide *spiro*-$N_3P_3[O_2C_{12}H_8][N(Me)NH_2]_4$ (**3**), which contains four terminal −NH_2 end groups (Scheme 1). The proton NMR spectrum of **3** shows a doublet (with strong virtual coupling)[13] for the N−CH_3 protons at 2.84 ppm. Four sets of equivalent protons of the biphenyloxy group are well resolved and show a first-order spectrum. The −NH_2 protons are seen as a broad peak centered at 3.5 ppm. The $^{31}P\{^1H\}$NMR spectrum of **3** is of the AB_2 type with the signal for *P*($O_2C_{12}H_8$) resonating at 27.2 ppm while *P*(N(Me)NH_2)$_2$ is seen at a higher frequency at 29.9 ppm. In the tetrachloro derivative **2** the signal for *P*($O_2C_{12}H_8$) is seen at 12.9 ppm while *P*Cl_2 is observed at

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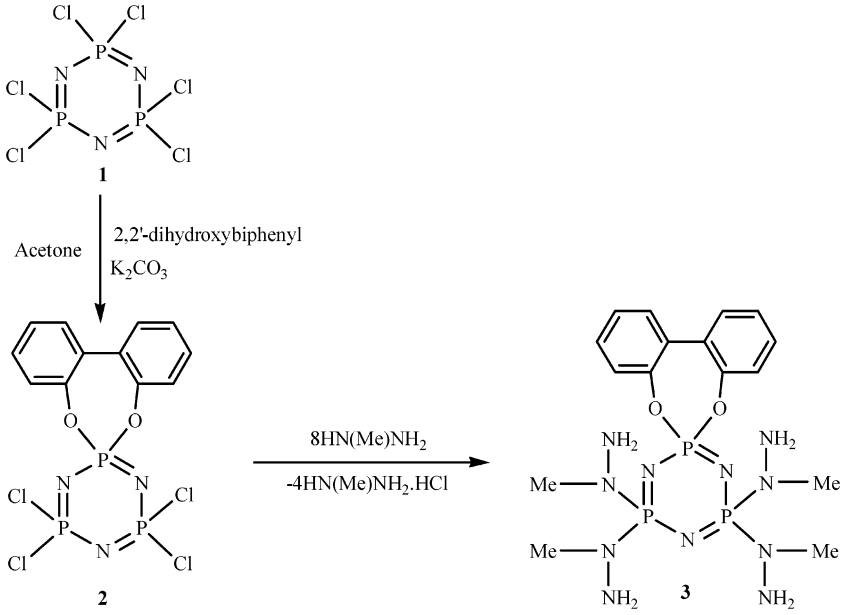
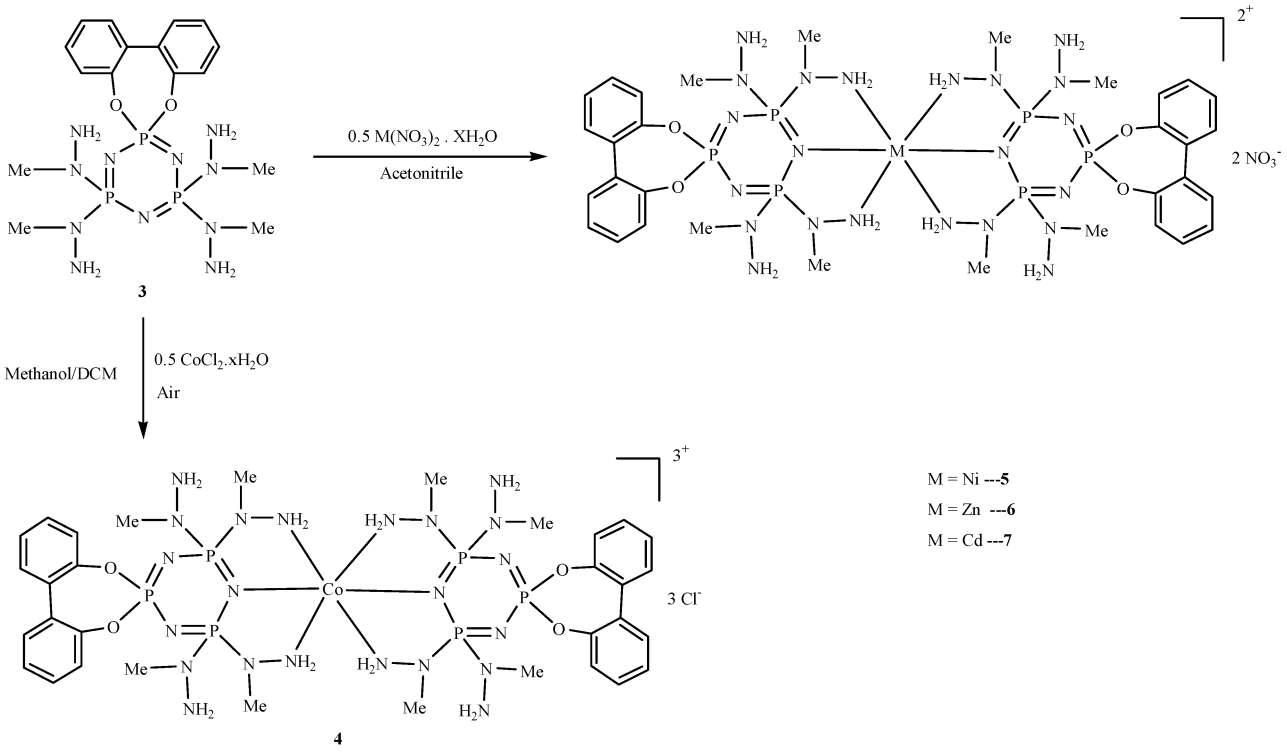
Scheme 1



Scheme 2



24.8 ppm. The ^2J(P−N−P) of 71.2 Hz seen in **2** is reduced to 53.4 Hz in **3**.

Reaction of **3** with hydrated metal salts directly affords the complexes **4**−**7** in which the cyclophosphazene hydrazide ligand is preserved in its entirety and does not suffer any degradation (Scheme 2). This is in sharp contrast to the hydrolytic sensitivity of the P−N bond in pyrazolyl cyclotriphosphazenes such as $N_3P_3(3,5\text{-}Me_2Pz)_6$[5c] as well as in acyclic phosphorus pyrazolide ligands such as $(O)P(3,5\text{-}Me_2Pz)_3$,[14] $MeP(S)(3,5\text{-}Me_2Pz)_2$,[15] $PhP(O)(3,5\text{-}Me_2Pz)_2$, and $Ph_2P(O)(3,5\text{-}Me_2Pz)$.[16] Interestingly, irrespective of the stoichiometry of the metal salt and the tetrahydrazide (**3**), only 2:1 complexes (L:M) were isolated. This may be compared with the failure to isolate *even* one such complex in the reactions with pyrazolyl cyclotriphosphazenes. The latter

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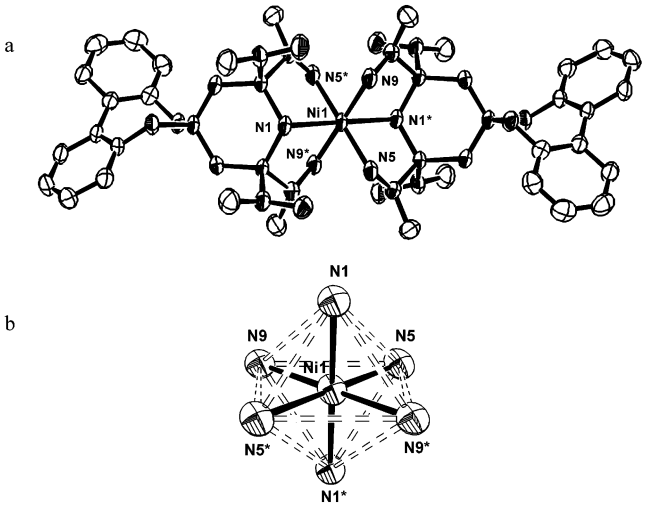


Figure 1. (a) ORTEP diagram of **5**. (The thermal ellipsoids are drawn at the 50% probability level.) Hydrogen atoms have been omitted for clarity. (b) Coordination environment around Ni(II).

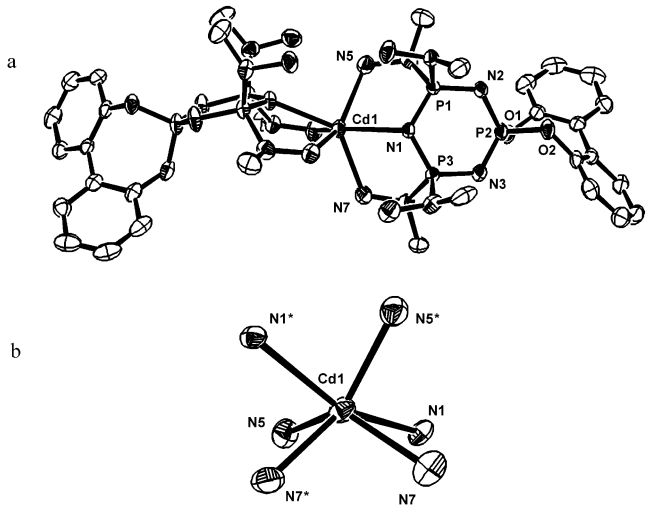


Figure 2. (a) ORTEP diagram of **7.** (The thermal ellipsoids are drawn at the 50% probability level.) Hydrogen atoms have been omitted for clarity. (b) Severely distorted coordination environment around Cd(II).

afforded 1:1 or 1:2 (L:M) complexes. The complexes **4**−**7** were characterized by a combination of analytical, spectroscopic, and X-ray crystallographic techniques. Interestingly, aerial oxidation was sufficient to oxidize cobalt to its +3 oxidation state in the complex **4**. Thus, complexes **4**, **6**, and **7** are diamagnetic while the Ni(II) derivative is paramagnetic with a μ_B of 2.92 μ_B. The complexes **4**, **6**, and **7** also showed an AB_2 type of ^{31}P NMR. In the Co(III) complex (**4**) the chemical shifts are most affected with $\delta[P(O_2C_{12}H_8)]$ resonating at 19.7 ppm while $\delta[P(N(Me)NH_2)_2]$ is seen at 35.4 ppm. The corresponding chemical shifts for the Zn(II) complex are 24.0 and 26.7 ppm while those of the Cd(II) complex are 24.6 and 26.4 ppm, respectively. The ν(P═N) seen in **3** at 1215 cm^{-1} is shifted to 1229 (**4**), 1224 (**5**), 1223 (**6**), and 1226 (**7**) cm^{-1} in the compounds **4**−**7**. Such a shift is attributable to the ring nitrogen of the cyclophosphazene being involved in coordination to the transition metal ion.[2] This estimate has been confirmed by the X-ray crystal structures of **4**−**7**.

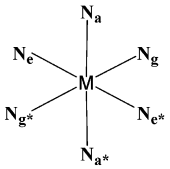
X-ray Crystal Structures of 4−**7**. The X-ray crystal structures of compounds **4**−**7** reveal that the metal ions in the complexes **4**−**6** have very similar coordination geometry and coordination environment. The X-ray crystal structure of the Cd(II) complex **7** reveals that although the coordination environment around the metal ion is the same as in the case of compounds **4**−**6**, the coordination geometry around Cd(II) is much more distorted from the ideal octahedron. Representative ORTEP diagrams for complexes **5** and **7** are given in Figures1 and 2, respectively. A summary of the metric parameters of the complexes **4**−**7** is given in Tables2−4.

In all the complexes (**4**−**7**) two cyclotriphosphazene ligands are involved in binding to a central metal ion. In all four structures it is seen that each cyclophosphazene molecule interacts with the metal ion through one ring nitrogen atom and two $-NH_2$ nitrogen atoms belonging to the *non-geminal-N*-methylhydrazine groups that flank the coordinating cyclophosphazene nitrogen atom. In the case of compounds **4**−**6** the coordination geometry around the metal ion is slightly distorted from a regular octahedron. In each case a facial disposition of the three nitrogen donor centers of the cyclophosphazene moiety is seen. Within the N_6 donor set around the metal ion, the two cyclophosphazene nitrogen atoms are trans with respect to each other. The *non-geminal*-N_3 coordination mode of the ligand in these complexes leads to the formation of a bicyclic ring made up of two interlinked five-membered PN_3M rings. The bicyclic ring thus formed assumes an *open-book* type of conformation where the dihedral angle between the two five-membered rings is around 134° (Figure 1a). In the complexes **4**−**6** the cyclotriphosphazene ring is very nearly planar, which suggests that the ligand **3** is able to coordinate to the metal ions Co(III), Ni(II), and Zn(II) without the need for major conformational changes of the cyclophosphazene ring.

The Cd(II) complex has a structure slightly different from those of **4**−**6**. Although, in this case also two cyclophosphazene rings are involved in coordination, each providing three nitrogen donor atoms (one ring nitrogen atom and two *non-geminal* hydrazido $-NH_2$ nitrogen atoms) the larger size of Cd(II) demands changes in coordination geometry as well as some structural reorganization in the cyclophosphazene ligand. Thus, the geometry around Cd(II) is severely distorted from a regular octahedron. The N1−M−N5, N1−M−N7, and N5−M−N7 angles in the Cd(II) complex are 74.84(12), 74.22(11), and 131.63(13)°. This may be compared with the corresponding angles for the Zn(II) complex which are 80.57(6), 80.70(6), and 92.37(6)° (Table 2).

A comparison of the metric parameters of the four complexes among themselves and with those of the parent ligand is quite instructive. (1) The $M-N_a$ distance is slightly longer than the corresponding $M-N_e$ and $M-N_g$ distances for each complex (Table 2). The maximum difference is seen in the Cd(II) complex **7**. (2) The longest $M-N_a$ distance is seen in the Cd(II) (**7**) derivative (2.428(3) Å) while the shortest distance is observed in the Co(III) complex (**4**) (1.993(12) Å). (3) The maximum variation in the cyclophosphazene ring P−N distances that flank the coordinating nitrogen is also seen for **4** (1.649(12) Å) (Table 3). For other complexes also there is a lengthening of this distance but

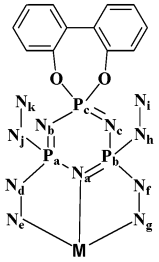
Table 2. Comparison of Bond Length (Å) and Angle (deg) Data for Compounds **4**−**7** around the Central Metal Ion[a]



	bond lengths			bond angles		
compd	M−N_a	M−N_e	M−N_g	N_a−M−N_e	N_a−M−N_g	N_e−M−N_g
4	1.993(12)	1.940(12)	1.946(13)	84.0(5)	83.3(5)	91.2(5)
5	2.135(3)	2.100(4)	2.106(4)	98.52(14)	98.21(14)	93.78(16)
6	2.189(15)	2.155(17)	2.159(17)	80.57(6)	80.70(6)	92.37(6)
7	2.428(3)	2.309(4)	2.367(4)	74.84(12)	74.22(11)	131.63(13)

[a] Average values. The largest esd is given. N_a, N_{a*} = cyclotriphosphazene ring nitrogen. N_e, N_{e*}, N_g, N_{g*} = hydrazide nitrogens

Table 3. Comparison of Bond Lengths (Å) for Compounds **3**−**7**[a]



compd	A	B	C	D	E	F	G
3[19]	1.572(6)	1.591(5)	1.550(6)	1.653(6)[b]		1.432(9)[c]	
4	1.649(12)	1.582(15)	1.569(14)	1.663(12)	1.633(13)	1.445(16)	1.418(2)
5	1.622(4)	1.593(4)	1.566(4)	1.664(4)	1.649(5)	1.438(6)	1.438(6)
6	1.617(16)	1.596(16)	1.572(17)	1.659(17)	1.654(18)	1.439(2)	1.431(2)
7	1.612(3)	1.584(4)	1.576(4)	1.656(4)	1.661(4)	1.423(5)	1.430(5)

[a] A = average of P_aN_a and P_bN_a; B = average of P_aN_b and P_bN_c; C = average of P_cN_b and P_cN_c; D = average of P_aN_d and P_bN_f; E = average of P_aN_j and P_bN_h; F = average of N_dN_e and N_fN_g; G = average of N_jN_k and N_hN_i. [b,c] In these case there is no difference between D,E and F,G.

Table 4. Comparison of Cyclophosphazene Bond Angles (deg) for Compounds **3**−**7**

compd	P_a−N_a−P_b	P_c−N_b−P_a	P_c−N_c−P_b	N_b−P_a−N_a	N_b−P_c−N_c	N_c−P_b−N_a
3[19]	123.7(3)	121.0(3)	121.4(3)	115.4(3)	120.5(3)	115.0(3)
4	120.2(8)	124.6(9)	124.0(8)	115.8(6)	117.5(7)	116.6(7)
5	122.1(2)	123.2(2)	124.0(2)	116.35(19)	118.2(2)	115.7(2)
6	123.5(1)	123.2(1)	122.2(10)	115.3(8)	119.0(8)	116.0(8)
7	121.35(17)	121.1(2)	122.1(2)	117.44(17)	118.22(19)	116.46(18)

by a slightly smaller amount. Such a P−N bond-length increase flanking the site of coordination or protonation is known from studies on cyclotriphosphazene metal complexes as well as protonated cyclophosphazenes.[1f,2b,5a] This is consistent with bonding model of Craig[17] and Paddock.[18] Accordingly, in such situations the lone pair on the ring nitrogen of the cyclophosphazene is not available for π-bonding interactions within the ring causing an increase of the affected bond distance. (4) The P−N−P angle is much less affected by ring nitrogen coordination (Table 4). (5) A slight lengthening of the N−N distances is noticed upon coordination. (6) The cyclophosphazene ring is nearly planar in **4**−**6** while in **7** deviation from planarity occurs. Thus, N1 deviates from the plane of the ring by about 0.1 Å.

In general it may be said that in comparison to the situation in metal complexes formed by pyrazolyl cyclotriphosphazenes, as for example, in $N_3P_3(3,5\text{-}Me_2Pz)_6\cdot CuCl_2$,[5c] where the cyclotriphosphazene ring is severely distorted, in the complexes formed with the tetrahydrazide ligand **3** the cyclophosphazene ring is not forced to undergo major deviation from planarity.

A further point of interest is that in all of the above complexes (**4**−**7**) the coordination of each of the cyclotriphosphazene ring is some what similar to that of the celebrated scorpionate family of ligands.[20] Thus, the claws

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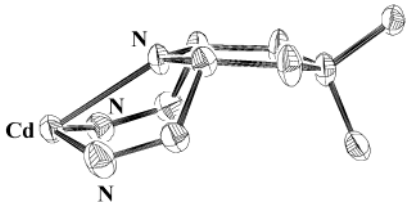

Figure 3. η^3-*non-geminal*-N_3 coordination mode of the ligand **3**.

of the scorpion are represented by the two *non-geminal* amino nitrogen atoms while the bite of the scorpion is provided by the cyclotriphosphazene ring nitrogen atom (Figure 3).

Conclusion

Cyclophosphazene-based tetrahydrazide *spiro*-$N_3P_3[O_2C_{12}H_8]$-$[N(Me)NH_2]_4$ (L) has been shown to be an efficient and robust multisite coordination ligand that affords complexes of the type $[L_2Co]^{3+}$ and $[L_2M]^{2+}$ (M = Ni, Zn, Cd). The cyclophosphazene utilizes two *non-eminal*-hydrazine $-NH_2$ nitrogen atoms along with a ring nitrogen atom to function as a η^3-*non-geminal*-N_3 donor.

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Supporting Information Available: Tables S1−S4, additional Figures S1−S6, 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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