

Cyclo- and Carbophosphazene-Supported Ligands for the Assembly of Heterometallic ($\text{Cu}^{2+}/\text{Ca}^{2+}$, $\text{Cu}^{2+}/\text{Dy}^{3+}$, $\text{Cu}^{2+}/\text{Tb}^{3+}$) Complexes: Synthesis, Structure, and Magnetism

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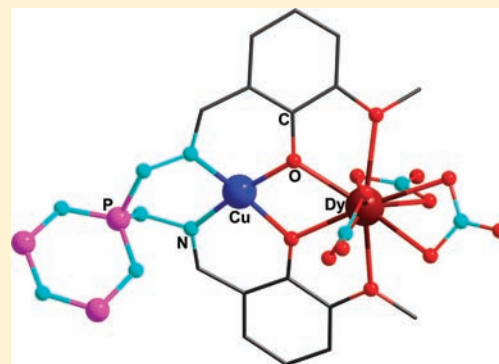
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Supporting Information

ABSTRACT: The carbophosphazene and cyclophosphazene hydrazides, $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{NH}_2\}_2}]$ (1) and $[\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_2\{\text{N}(\text{CH}_3)\text{NH}_2\}_2]$ were condensed with *o*-vanillin to afford the multisite coordination ligands $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)\}_2}]$ (2) and $[\{\text{N}_2\text{P}_2(\text{O}_2\text{C}_{12}\text{H}_8)_2\}\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)\}_2}]$ (3), respectively. These ligands were used for the preparation of heterometallic complexes $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)\}_2]\{\text{CuCa}(\text{NO}_3)_2\}$ (4), $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)\}_2]\{\text{Cu}_2\text{Ca}_2(\text{NO}_3)_4\}\cdot 4\text{H}_2\text{O}$ (5), $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)\}_2]\{\text{CuDy}(\text{NO}_3)_4\}\cdot \text{CH}_3\text{COCH}_3$ (6), $[\{\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)_2\}\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)\}_2]\{\text{CuDy}(\text{NO}_3)_3\}$ (7), and $[\{\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)_2\}\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)\}_2]\{\text{CuTb}(\text{NO}_3)_3\}$ (8). The molecular structures of these compounds reveals that the ligands 2 and 3 possess dual coordination pockets which are used to specifically bind the transition metal ion and the alkaline earth/lanthanide metal ion; the $\text{Cu}^{2+}/\text{Ca}^{2+}$, $\text{Cu}^{2+}/\text{Tb}^{3+}$, and $\text{Cu}^{2+}/\text{Dy}^{3+}$ pairs in these compounds are brought together by phenoxide and methoxy oxygen atoms. While 4, 6, 7, and 8 are dinuclear complexes, 5 is a tetranuclear complex. Detailed magnetic properties on 6–8 reveal that these compounds show weak couplings between the magnetic centers and magnetic anisotropy. However, the ac susceptibility experiments did not reveal any out of phase signal suggesting that in these compounds slow relaxation of magnetization is absent above 1.8 K.



INTRODUCTION

Cyclophosphazenes are an important class of inorganic heterocyclic ring compounds and have attracted interest because of various reasons such as their structure and reactivity as well as their relationship to inorganic polymer chemistry.^{1–3} For some years, we and others have been examining the possibility of using these heterocyclic compounds as scaffolds for preparing multisite coordination ligands.^{4–7} While we have been using the reactivity of compounds such as $\text{N}_3\text{P}_3\text{Cl}_6$ to study nucleophilic substitution reactions at the phosphorus with appropriate nucleophiles to design coordinating ligands,^{4–7} others, notably Steiner and co-workers have used polyanionic phosphazenes and zwitterionic phosphazanium phosphazenes as versatile ligands.⁷ In addition, there has also been interest to use cyclophosphazenes as dendrimer-like star-shaped molecules containing interesting functional units in the periphery.⁸ In this domain, Majoral and co-workers have pioneered the use of cyclophosphazenes in dendrimer chemistry.⁹

Recently, we have been interested in developing ligands that would have specific coordination sites to chelate both 3d and 4f metal ions to obtain heterometallic complexes with interesting magnetic properties.¹⁰ So far, all the ligands used for such a purpose have been based on an acyclic phosphorus "platform".^{10b–e} We were interested to examine if the inorganic heterocyclic rings cyclocarbophosphazenes and cyclophosphazenes can be tailored to afford multisite coordination capabilities in such a way that specific heterometallic assemblies could be readily built. Accordingly, we used the phosphorus hydrazide precursors, $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{NH}_2\}_2}]$ (1) and $[\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_2\{\text{N}(\text{CH}_3)\text{NH}_2\}_2]$ to build multisite coordination ligands $[\{\text{NC}(\text{N}(\text{CH}_3)_2)\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)\}_2}]$ (2) and $[\{\text{N}_2\text{P}_2(\text{O}_2\text{C}_{12}\text{H}_8)_2\}\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)\}_2}]$ (3), respectively. These ligands were used for the

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preparation of heterometallic dinuclear complexes containing $\text{Cu}^{2+}/\text{Ca}^{2+}$, $\text{Cu}^{2+}/\text{Dy}^{3+}$, and $\text{Cu}^{2+}/\text{Tb}^{3+}$ units. While the $\text{Cu}^{2+}/\text{Dy}^{3+}$ and $\text{Cu}^{2+}/\text{Tb}^{3+}$ systems were chosen for their interest in magnetism, we examined the $\text{Cu}^{2+}/\text{Ca}^{2+}$ system with a view to examine the coordination sites of **2** and **3** in particular keeping in mind that the Ca^{2+} coordination is usually very similar to that of the lanthanide ions. Accordingly in this paper we describe the synthesis and X-ray structural characterization of the ligands, **2** and **3**, together with the heterometallic complexes, $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{CuCa}(\text{NO}_3)_2\}]$ (**4**), $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{Cu}_2\text{Ca}_2(\text{NO}_3)_4\}]\cdot 4\text{H}_2\text{O}$ (**5**), $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{CuDy}(\text{NO}_3)_3\}]\cdot \text{C}_6\text{H}_3\text{COCH}_3$ (**6**), $[\{\text{NP}(\text{O}_2\text{C}_2\text{H}_5)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{CuDy}(\text{NO}_3)_3\}]$ (**7**), and $[\{\text{NP}(\text{O}_2\text{C}_2\text{H}_5)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{CuTb}(\text{NO}_3)_3\}]$ (**8**). While **4**, **6**, **7**, and **8** are dinuclear complexes, **5** is a tetranuclear complex. The detailed magnetic properties of **6–8** are also reported.

EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.¹¹ $\text{NaN}(\text{CN})_2$ and 4-hydroxy-pyridine (Fluka, Switzerland), PCl_5 (s. d. Fine Chemicals, India), pyridine (s. d. Fine Chemicals, India), and $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (Sigma Aldrich, U.S.A.), were used as purchased. $[\text{NCCl}_2][\text{NPCL}_2]$,¹¹ N,N,N',N' -tetramethylmethylenediamine,¹² $[\text{NC}(\text{N}(\text{CH}_3)_2)_2][\text{NPCL}_2]$,¹³ and $[\text{N}_3\text{P}_3(\text{O}_2\text{C}_2\text{H}_5)_2][\text{N}(\text{CH}_3)\text{NH}_2]_2$ ¹⁴ were prepared according to literature procedures.

Instrumentation. Melting points were measured using a JSGW apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to 4000 cm^{-1} . ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. The ionization mechanism used was electrospray in positive ion full scan mode using methanol as solvent and nitrogen gas for desolvation. The capillary voltage of the machine was maintained at 3 kV, and the cone voltage was kept at 30 V. The temperature maintained for ion source was $100\text{ }^\circ\text{C}$ and for desolvation at $250\text{ }^\circ\text{C}$. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 solutions on a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0 and 161.7 MHz, respectively. Chemical shifts are reported in parts per million (ppm) and referenced with respect to internal tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P).

Magnetic Measurements. The magnetic susceptibility measurements were obtained with the use of a MPMS-XL Quantum Design SQUID magnetometer. This magnetometer works between 1.8 and 400 K for direct current (dc) applied fields ranging from -7 to 7 T. Measurements were performed on polycrystalline samples of 16.55, 18.16, and 17.7 mg for **6**, **7**, and **8**, respectively, introduced in a polyethylene bag ($3 \times 0.5 \times 0.02\text{ cm}$). Alternating current (ac) susceptibility measurements were measured with an oscillating ac field of 3 Oe with frequency between 1 to 1500 Hz. It is worth noting that no out-of-phase ac susceptibility signal has been detected above 1.8 K. The magnetic data were corrected for the sample holder (polyethylene bag) and the diamagnetic contribution.

Synthesis. $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{NH}_2\}_2\}]$ (**1**). To a solution of $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NPCL}_2\}]$ (4.71 g, 18.2 mmol) in dry chloroform (70 mL), $\text{HN}(\text{CH}_3)\text{NH}_2$ (3.98 mL, 74.9 mmol) in 30 mL of chloroform was added dropwise at $0\text{ }^\circ\text{C}$ and stirred for 24 h at room temperature. The salt $\text{HN}(\text{CH}_3)\text{NH}_2\cdot\text{HCl}$ precipitated out of the solvent. The solution was filtered, and removal of solvent from the filtrate afforded a solid product. The latter was dissolved in hot acetonitrile (60 mL) and

allowed to come to $25\text{ }^\circ\text{C}$ affording a white crystalline solid. Yield: 4.1 g, 80.7% (based on phosphorus). ^1H NMR (CDCl_3 , δ): 2.80 (d, 6H, $-\text{N}(\text{CH}_3)\text{NH}_2$), 3.07 (s, 6H, $-\text{N}(\text{CH}_3)_2$), 3.67 (s(broad), 4H, $-\text{NH}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 42.0 (s). IR (KBr) cm^{-1} : 3315 (b), 2958 (m), 2927 (m), 2866 (m), 1578 (s), 1490 (m), 1436 (m), 1352 (s), 1264 (s), 1219 (m), 1093 (s), 1022 (m), 940 (m), 717 (m). ESI-MS m/z , ion: 276.18. Anal. Calcd for $\text{C}_8\text{H}_{22}\text{N}_6\text{P}$ (275.17): C, 34.90; H, 8.05; N, 45.79. Found: C, 34.95; H, 8.06; N, 45.73.

$[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)_2\}\}]$ (**2**). To a solution of $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{NH}_2\}_2\}]$ (6.7 g, 24.3 mmol) in dry ethanol (50 mL) at room temperature an ethanolic solution (20 mL) of *o*-vanillin (7.40 g, 48.6 mmol) was added dropwise. After the addition was complete, the reaction mixture was refluxed for 24 h. **2** precipitated as a white residue which was separated by filtration through a G-4 open frit. The precipitate was washed with cold ethanol, followed by diethyl ether and air-dried. Yield: 11.7 g, 88.4% (based on phosphorus). Mp: $190\text{ }^\circ\text{C}$. IR (KBr) cm^{-1} : 3422 (b), 2996 (w), 2931 (m), 1605 (s), 1546 (s), 1513 (m), 1484 (s), 1464 (s), 1401 (m), 1365 (s), 1266 (s), 1252 (s), 1243 (s), 1156 (s), 1078 (s), 1064 (s), 974 (s), 936 (s), 914 (s), 878 (w), 838 (m), 766 (m), 738 (m), 708 (s), 613 (m), 523 (m), 491 (m). ESI-MS m/z , ion: 544.25. Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_6\text{O}_4\text{P}$ (543.25): C, 53.03; H, 6.30; N, 23.19. Found: C, 53.10; H, 6.36; N, 23.15. ^1H NMR (CDCl_3 , δ): 7.64 (s, 2H, $-\text{CH}=\text{N}$), 6.77 (m, 6H, aromatic), 3.89 (s, 6H, $-\text{OCH}_3$) and 3.24 (s, 6H, $-\text{NCH}_3$), 3.08 (s, 12H, $-\text{N}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 34.26 (s).

$[\{\text{N}_2\text{P}_2(\text{O}_2\text{C}_2\text{H}_5)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)_2\}\}]$ (**3**). To a solution of $\text{N}_3\text{P}_3(\text{O}_2\text{C}_2\text{H}_5)_2[\text{N}(\text{CH}_3)\text{NH}_2]_2$ (4.06 g, 6.8 mmol), in dry ethanol (60 mL), at room temperature, an ethanolic solution (20 mL) of *o*-vanillin (2.10 g, 13.8 mmol) was added dropwise. After the addition was completed, the reaction mixture was stirred for 12 h at room temperature. Ligand **3** was obtained as a white precipitate. It was separated out by filtration through a G-4 open frit. The precipitate was washed by cold ethanol and dried. Anal. Calcd for $\text{C}_{42}\text{H}_{58}\text{N}_7\text{O}_8\text{P}_3$ (861.20): C, 58.54; H, 4.44; N, 11.38; Found: C, 59.21; H, 4.42; N, 10.93. This was recrystallized from ethanol/chloroform/toluene (3:3:1) mixture and air-dried. Yield: 4.59 g, 77.86% (based on phosphorus). Mp: $180\text{ }^\circ\text{C}$. IR (KBr) cm^{-1} : 3433 (b), 3063 (w), 2933 (w), 1602 (m), 1573 (m), 1498 (s), 1469 (s), 1438 (m), 1378 (s), 1269 (s), 1250 (s), 1228 (s), 1196 (s), 1172 (s), 1002 (m), 926 (s), 881 (s), 757 (s), 696 (s), 609 (s), 587 (s), 535 (m), 489 (s). ESI-MS m/z , ion: 862.21. Anal. Calcd for $(3\cdot 3\text{C}_6\text{H}_5\text{CH}_3\cdot 2\text{H}_2\text{O})\text{C}_{63}\text{H}_{66}\text{N}_7\text{O}_{10}\text{P}_3$ (1174.16): C, 64.44; H, 5.67; N, 8.35. Found: C, 64.05; H, 5.06; N, 8.81. ^1H NMR (CDCl_3 , δ): 10.95 (s, 2H, $-\text{CH}=\text{N}$), 7.64–6.69 (m, 24H aromatic), 3.82 (s, 6H, $-\text{OCH}_3$) and 3.43 (s, 6H, $-\text{N}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 25.56 (d, $\text{P}(\text{O}_2\text{C}_2\text{H}_5)_2$), 17.73 (t, $\text{P}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)_2\}$).

Preparation of Complexes 4–8. A general procedure was applied for the preparation of **4–8**. To a solution of the hydrazone ligand in methanol (30 mL), $\text{CuX}_2\cdot n\text{H}_2\text{O}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- ; $n = 1, 3$) and $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ or $\text{Ln}(\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Dy}, \text{Tb}$; $n = 3, 5$) were added. The reaction mixture was stirred for 6 h to afford a clear solution. This was filtered and the filtrate evaporated to dryness. The residue obtained was washed with diethyl ether and dried. The residue was dissolved in methanol/chloroform (1:1) (For **4** and **5**), methanol/acetone (1:1) (For **6**), methanol/acetonitrile (1:1) (For **7** and **8**) and kept for crystallization. After 3–7 days, pure crystalline products were isolated. Specific details of each reaction and the characterization data of the products obtained are given below.

$[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-O})(m\text{-OCH}_3)_2\}\}\{\text{CuCa}(\text{NO}_3)_2\}](\text{H}_2\text{O})(\text{CHCl}_3)$ (**4**). Quantities: $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (0.04 g, 0.18 mmol), $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.04 g, 0.18 mmol) and $[\{\text{NC}(\text{N}(\text{CH}_3)_2)_2\}_2\{\text{NP}\{\text{N}(\text{CH}_3)\text{N}=\text{CH}-\text{C}_6\text{H}_3-(o\text{-OH})(m\text{-OCH}_3)_2\}\}]$ (0.10 g, 0.18 mmol). Yield: 0.12 g, 68.8% (based on phosphorus). Mp: $230\text{ }^\circ\text{C}$. IR (KBr) cm^{-1} : 3399 (b), 2924 (m), 2852 (w), 2151 (w), 1706 (m), 1608 (s), 1552 (w), 1516 (s), 1459 (s), 1370 (s), 1311 (s), 1243 (m), 1217 (s), 1172 (m), 1124 (m), 1030 (s), 976 (s), 858 (m), 778 (m), 723 (m), 605 (m), 550 (m), 499 (m). ESI-MS m/z , ion: 706.06, $[\text{CuCa}(\text{C}_{24}\text{H}_{32}\text{N}_6\text{O}_4\text{P})(\text{NO}_3)]^+$. Anal. Calcd for solvent free

sample obtained by drying in vacuum (10^{-3} Torr) for 6 h: $C_{24}H_{36}CaCuN_{11}O_{12}P$ (805.21): C, 35.80; H, 4.51; N, 19.13. Found: C, 35.72; H, 3.88; N, 18.09.

$[\{NC(N(CH_3)_2)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-O)(m-OCH_3)\}_2\}\{Cu_2Ca_2(NO_3)_4\}\cdot 4H_2O$ (**5**). Quantities: $Cu(NO_3)_2\cdot 3H_2O$ (0.05 g, 0.19 mmol), $Ca(NO_3)_2\cdot 4H_2O$ (0.04 g, 0.19 mmol) and $[\{NC(N(CH_3)_2)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-OH)(m-OCH_3)\}_2\}]$ (0.10 g, 0.19 mmol). Yield: 0.11 g, 72.0% (based on phosphorus). Mp: 280 °C. IR (KBr) cm^{-1} : 3404 (b), 3059 (m), 2946 (w), 1948 (m), 1706 (w), 1665 (s), 1607 (s), 1535 (w), 1468 (s), 1405 (w), 1370 (s), 1311 (s), 1243 (m), 1173 (s), 1068 (m), 976 (s), 936 (s), 880 (m), 793 (m), 740 (m), 605 (m), 550 (m), 515 (m). ESI-MS m/z , ion: 706.06 $[CuCa(C_{24}H_{32}N_9O_4P)(NO_3)]^+$. Anal. Calcd for $C_{48}H_{76}Ca_2Cu_2N_{22}O_{26}P_2$ (1646.44): C, 35.02; H, 4.65; N, 18.72. Found: C, 35.10; H, 4.69; N, 18.69.

$[\{NC(N(CH_3)_2)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-O)(m-OCH_3)\}_2\}\{CuDy(NO_3)_4\}\cdot CH_3COH_3$ (**6**). Quantities: $Cu(OAc)_2\cdot H_2O$ (0.07 g, 0.37 mmol), $[\{NC(N(CH_3)_2)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-OH)(m-OCH_3)\}_2\}]$ (0.20 g, 0.37 mmol), $Dy(NO_3)_3\cdot 5H_2O$ (0.16 g, 0.37 mmol). Yield: 0.280 g, 70.7% (based on phosphorus). Mp: > 300 °C. IR (KBr) cm^{-1} : 3160 (w), 3061 (w), 2948 (m), 1714 (m), 1627 (s), 1556 (m), 1465 (s), 1385 (s), 1320 (s), 1223 (s), 1170 (m), 1060 (s), 962 (s), 928 (m), 814 (m), 737 (s), 647 (m), 625 (m), 584 (m), 530 (m), 497 (m). ESI-MS m/z , ion: 892.03 $[CuDy(C_{24}H_{32}N_9O_4P)(NO_3)_2]^+$. Anal. Calcd for $C_{27}H_{39}CuDyN_{13}O_{17}P$ (1074.70): C, 30.17; H, 3.66; N, 16.94. Found: C, 30.21; H, 3.71; N, 16.83.

$[\{NP(O_2C_{12}H_8)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-O)(m-OCH_3)\}_2\}\{CuDy(NO_3)_3\}\cdot CH_3CN$ (**7**). Quantities: $Cu(OAc)_2\cdot H_2O$ (0.05 g, 0.23 mmol), $Dy(NO_3)_3\cdot 5H_2O$ (0.10 g, 0.23 mmol) and $[\{NP(O_2C_{12}H_8)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-OH)(m-OCH_3)\}_2\}]$ (0.20 g, 0.23 mmol). Yield: 0.21 g, 67.7% (based on phosphorus). Mp: > 300 °C. IR (KBr) cm^{-1} : 3405 (b), 3065 (w), 2926 (w), 2288 (w), 1610 (s), 1558 (w), 1510 (s), 1472 (s), 1439 (s), 1384 (w), 1297 (s), 1225 (s), 1170 (s), 1092 (s), 1028 (m), 966 (s), 914 (s), 822 (m), 782 (s), 718 (s), 631 (s), 587 (s), 530 (s), 466 (s). ESI-MS m/z , ion: 1287.04 $[CuDy(C_{42}H_{37}N_7O_8P_3)(NO_3)_3]^+$. Anal. Calcd for $C_{46}H_{42}CuDyN_{12}O_{17}P_3$ (1353.86): C, 40.81; H, 3.13; N, 12.41. Found: C, 40.91; H, 3.17; N, 12.37.

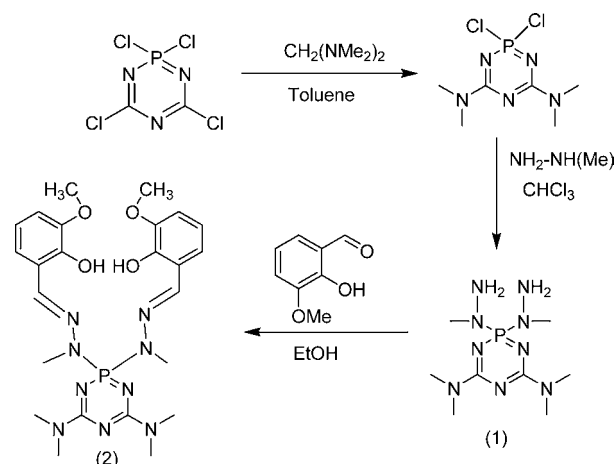
$[\{NP(O_2C_{12}H_8)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-O)(m-OCH_3)\}_2\}\{CuTb(NO_3)_3\}\cdot CH_3CN$ (**8**). Quantities: $Cu(OAc)_2\cdot H_2O$ (0.05 g, 0.23 mmol), $Tb(NO_3)_3\cdot 5H_2O$ (0.10 g, 0.23 mmol) and $[\{NP(O_2C_{12}H_8)\}_2\{NP\{N(CH_3)N=CH-C_6H_3-(o-OH)(m-OCH_3)\}_2\}]$ (0.200 g, 0.23 mmol). Yield: 0.22 g, 69.2% (based on phosphorus). Mp: > 300 °C. IR (KBr) cm^{-1} : 3423 (b), 3070 (w), 2925 (m), 2866 (m), 1602 (s), 1563 (w), 1502 (s), 1474 (s), 1439 (s), 1385 (w), 1301 (s), 1227 (s), 1174 (s), 1093 (s), 1015 (w), 967 (s), 914 (s), 880 (s), 823 (m), 755 (s), 718 (w), 609 (s), 535 (s). ESI-MS m/z , ion: 1282.04 $[CuTb(C_{42}H_{37}N_7O_8P_3)(NO_3)_3]^+$. Anal. Calcd for $C_{46}H_{42}CuN_{12}O_{17}P_3Tb$ (1350.29): C, 40.92; H, 3.14; N, 12.45. Found: C, 41.02; H, 3.16; N, 12.33.

X-ray Crystallography. The crystal data for the compounds have been collected on a Bruker SMART CCD diffractometer (MoK α radiation, $\lambda = 0.71073$ Å). The program SMART^{15a} was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT^{15a} for integration of the intensity of reflections and scaling, SADABS^{15b} for absorption correction, and SHELXTL^{15cd} for space group and structure determination and least-squares refinements on F^2 . All the structures were solved by direct methods using the program SHELXS-97^{15e} and refined by full-matrix least-squares methods against F^2 with SHELXL-97.^{15e} Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic figures have been generated using Diamond 3.1e software.^{15f} The crystal data and the cell parameters for compounds 2–8 are summarized in Supporting Information, Tables S1 and S2.

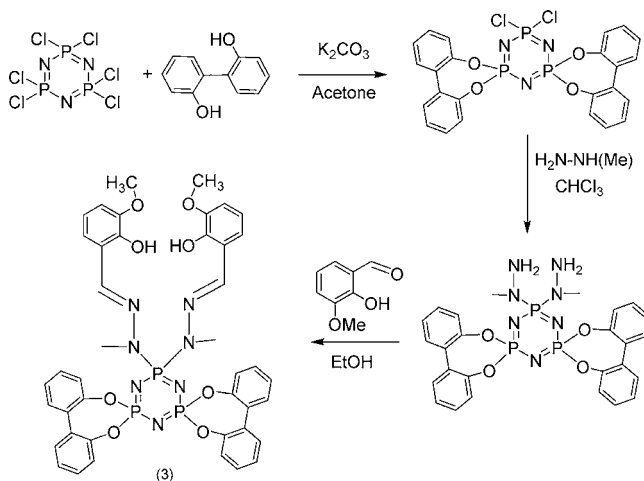
RESULTS AND DISCUSSION

Synthetic Aspects. The reactions of the dichlorocarbonyl and cyclophosphazenes, $[\{NC(N(CH_3)_2)\}_2\{NP(Cl)_2\}]$ and $N_3P_3(O_2C_{12}H_8)_2Cl_2$, with *N*-methylhydrazine occur in a regioselective manner affording the corresponding dihydrazides $[\{NC(NMe_2)\}_2\{NP\{N(CH_3)NH_2\}_2\}]$ (**1**) and $N_3P_3(O_2C_{12}H_8)_2[N(CH_3)NH_2]_2$ (Schemes 1 and 2). In these

Scheme 1. Synthesis of 1 and 2



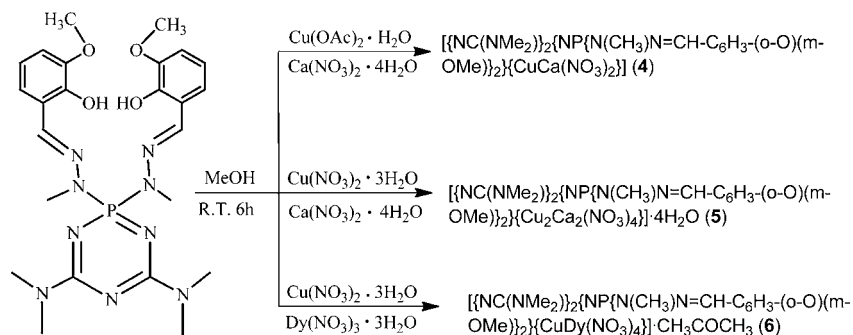
Scheme 2. Synthesis of 3



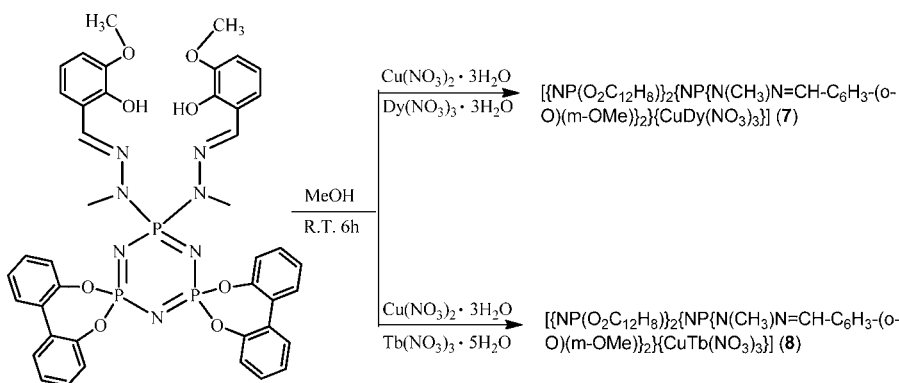
reactions, *N*-methylhydrazine itself has been used as the hydrogen chloride scavenger. Condensation of the dihydrazides $[\{NC(NMe_2)\}_2\{NP\{N(CH_3)NH_2\}_2\}]$ (**1**) and $N_3P_3(O_2C_{12}H_8)_2[N(CH_3)NH_2]_2$ with *o*-vanillin afforded the bishydrazones **2** and **3** in excellent yields (Schemes 1 and 2). The $^{31}P\{^1H\}$ NMR of the bishydrazones are upfield shifted in comparison to the bishydrazides $[NC(N(CH_3)_2)]_2[NP\{N(CH_3)NH_2\}_2]$ (see Experimental Section). This trend is similar to that found earlier in literature.¹⁶ The $N-CH_3$ chemical shifts of the hydrazones are downfield shifted in comparison to the hydrazones (see Experimental Section). ESI-MS of **1**–**3** reveal prominent parent ion peaks at m/z 276.18, 544.25, and 862.21, respectively. The molecular structures of **2**–**3** have been confirmed by X-ray crystallography (vide infra).

A 1:1:1 reaction of **2** with $Cu(OAc)_2\cdot H_2O$ and $Ca(NO_3)_2\cdot 4H_2O$ resulted in the formation of the heterometallic dinuclear complex **4** (Scheme 3). On the other hand, the use of

Scheme 3. Synthesis of the Heterometallic Complexes 4–6



Scheme 4. Synthesis of the Heterometallic Complexes 7–8



the copper nitrate salt affords the tetramer **5** (Scheme 3). The ESI-MS of **4** reveals a peak at 706.06 due to the $[\text{M}-\text{NO}_3]$ fragment of **4**. Interestingly the same peak is obtained for **5** also, suggesting that this compound breaks down into the monomer in solution. The reaction of **2** with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ afforded the 3d/4f complex **6** (Scheme 3). ESI-MS of the latter shows a peak at 892.03 corresponding to the unit $[\text{M}-2\text{NO}_3]$. The reactions of the cyclophosphazene hydrazone **3** with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ or $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ afforded the 3d/4f complexes **7** and **8**, respectively (Scheme 4). These compounds showed prominent parent ion peaks at 1287.04 and 1282.04 respectively in their ESI-MS.

Molecular Structures. *Dihydrazones 2 and 3.* The molecular structures of the dihydrazones **2** and **3** are shown in Supporting Information, Figure S2. Selected bond distances and angles of these molecules are summarized in Supporting Information, Table S15. The cyclocarbophosphazene ring in **2** is nearly planar (Supporting Information). The ring P–N bond lengths are similar and so are the ring C–N bond distances (Supporting Information, Table S15). The exocyclic P–N distances are longer in comparison to the ring P–N distance; however, the exocyclic C–N distances are not very different than the corresponding ring distances. The N1–P1–N2 angle $[114.4(1)^\circ]$ is smaller than the corresponding ring angles at carbon $[128.0(2)^\circ]$. The ring angles at nitrogen $[115.3(2), 115.1(2), \text{and } 118.9(2)^\circ]$ are closer to the angles anticipated at an sp^2 atom.

The cyclophosphazene ring in **3** is also nearly planar with only N3 deviating from the mean plane of the ring by -1.0 \AA (Supporting Information). Two of the ring P–N bond distances, P2–N1 and P1–N3 $[1.589(4) \text{ and } 1.588(3)]$, are slightly longer than the other ring P–N bond distances. As in

the case of **2**, the exocyclic P–N bond distances $[1.670(4) \text{ and } 1.666(3)]$ are substantially longer than the ring bond distances. In **3**, the endocyclic angles at nitrogen are larger than the endocyclic angles at phosphorus (Supporting Information, Table S15). Over all, the metric parameters and the structural features of **2** and **3** are in line with the general trends found in these families of compounds.

2 and **3** possess two distinct coordination pockets (Supporting Information, Figure S1). The inner pocket (P1) contains two imine nitrogen and two phenolic oxygen atoms while the outer pocket (P2) contains two methoxy and two phenolic oxygens. It can be anticipated from the geometry of **2** and **3** that the transition metal ion (Cu^{2+}) will be bound in P1 while Ca^{2+} , Dy^{3+} , or Tb^{3+} will occupy P2.

Heterometallic Complexes 4–8. The molecular structure of **4** is shown in Figure 1. Selected bond distances and angles of

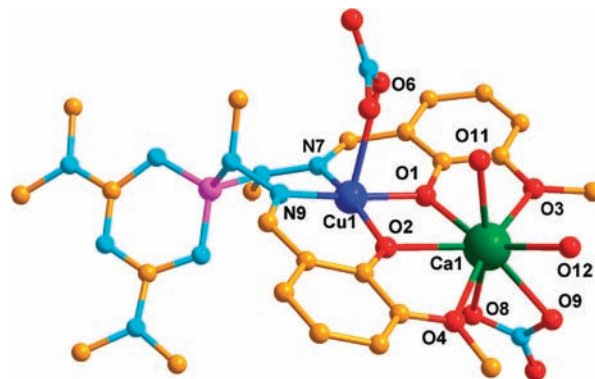


Figure 1. Molecular structure of **4**.

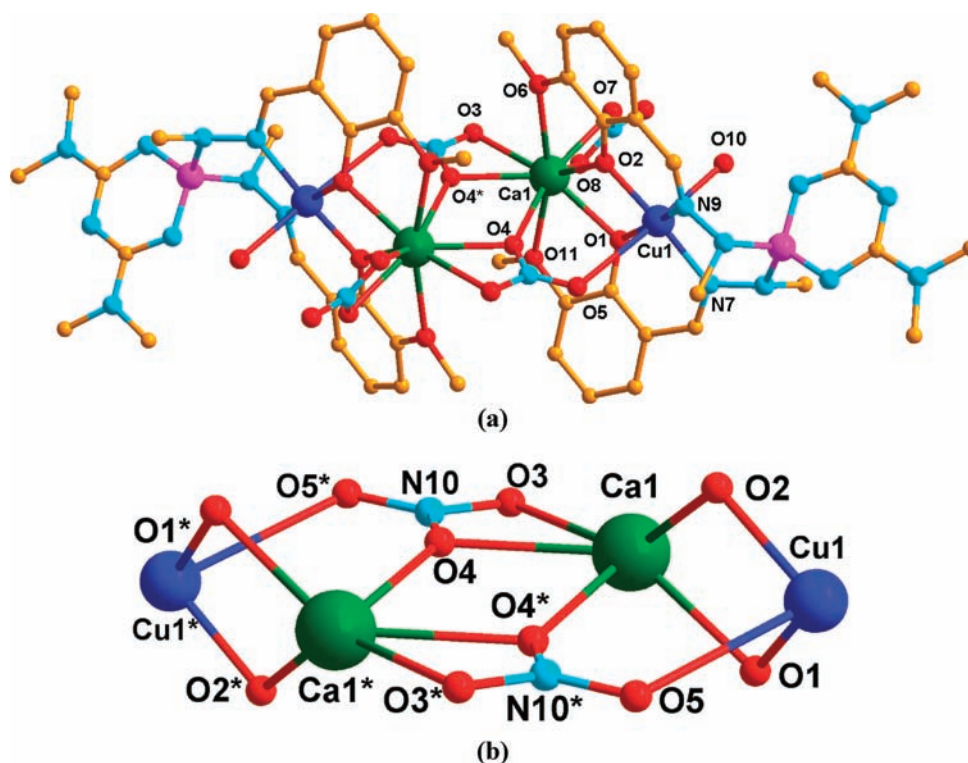


Figure 2. (a) Molecular structure of **5**. (b) The tetranuclear core of **5**.

this compound are summarized in Supporting Information, Table S16. In **4**, copper occupies the inner pocket (2N, 3O) while calcium occupies the outer pocket of the hydrazone ligand. The two metal ions in **4** are doubly bridged to each other by the phenoxido oxygen atoms O1 and O2, with a Cu...Ca distance of 3.462 (2) Å. The four-membered CaCuO₂ ring is nearly planar with O2 being out of the plane by 0.13 Å (Supporting Information). The bond angles at O1 and O2 are 107.7(2)° and 107.0(2)°, respectively. Copper is surrounded by five donor atoms (2N, 3O) in a distorted square pyramidal geometry. The equatorial N₂O₂ donor atoms are provided by the hydrazone ligand and are nearly coplanar while the axial position is occupied by the nitrate oxygen atom. The M-L distances in the equatorial plane [Cu1–O1, 1.907(4); Cu1–O2, 1.893(5); Cu1–N7, 1.994(6) and Cu1–N9, 1.944(5) Å] are substantially shorter than the axial Cu1–O6 distance of 2.833(7) Å. The bond angles around copper (Supporting Information, Table S16) are in line with the slight distortion of the square pyramidal geometry.

The calcium ion encapsulated in the outer coordination pocket P2, is eight-coordinated and is part of two five-membered and two four-membered rings (Figure 1). Ca1 is surrounded by an all-oxygen environment, and its coordination geometry can be described as distorted square antiprism (Supporting Information). Four of these eight coordinating oxygen atoms are derived from the hydrazone ligand and involve two bridging phenoxido oxygen atoms and two methoxy oxygen atoms. The other four oxygen atoms are provided by a chelating isobidentate nitrate ligand and two coordinating water molecules.

Among the various Ca–O bond distances, those involving the coordinating methoxy groups are the longest [2.502(5) and 2.530(5) Å] while those involving the phenoxido oxygen atoms and the water molecules are the shortest (Supporting

Information, Table S16); the Ca–O distances resulting from the chelating nitrate group are intermediate, 2.489(6) and 2.467(5) Å, respectively. Comparing the ring planarity (Supporting Information) as well as the metric parameters between the uncoordinated ligand and ligand in **4** (Supporting Information, Table S16), it appears that the carbophosphazene ring does not suffer any structural distortion even after the formation of the dinuclear complex.

Single crystal X-ray diffractions study reveals that **5** is a tetranuclear assembly (Figure 2a) that is composed of two dinuclear units, analogous to that found in **4**, bridged by two nitrate oxygens (O4 and O4*). The general structure of the dinuclear moiety in **4** and **5** is similar in both cases, the occupation of the coordination pockets by Cu²⁺ and Ca²⁺ metal ions. Nevertheless, there are some important differences between the two compounds. In **5**, the nitrate anions are involved in multiple coordination functions: (a) each nitrate functions as a chelating ligand to a calcium ion; (b) each nitrate is involved in pairing the two calcium centers belonging neighboring dinuclear complexes; (c) an oxygen of the nitrate ions is also coordinating to the copper center (Figure 2b). As a result, Cu1 is hexacoordinated (2N, 4O) possessing a distorted octahedral geometry with the two imine nitrogen atoms in cis configuration (Supporting Information). Each calcium atom in **5** is nonacoordinated in a capped trigonal antiprismatic geometry (Supporting Information). The all-oxygen Ca coordination sphere contains four oxygens from the hydrazone ligand and the remaining from the coordinating nitrate anions. The core structure of the tetranuclear unit is shown in Figure 2b. The coordination environment, selected bond distance and angles around the metal centers in **5** are given in Supporting Information, Table S17.

The molecular structure of the neutral 3d-4f bimetallic complex, {[NC(N(CH₃)₂)₂]₂[HNP{N(CH₃)N=CH-C₆H₃-(*o*-

O)(*m*-OCH₃)₂CuDy(NO₃)₄]}·(CH₃COCH₃) (6) (Figure 3) is only slightly different from that of 4. Selected bond distances

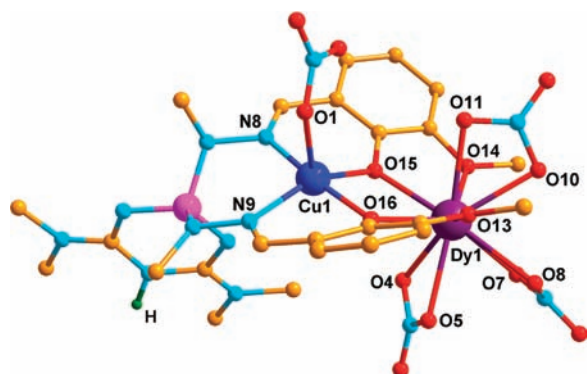


Figure 3. Molecular structure of 6.

and angles of this compound are summarized in Supporting Information, Table S18. In this complex, dysprosium is present as the second metal ions in replacement of the Ca(II) found in 4. Interestingly in 6, one of the ring nitrogen atoms (N2) of the carbophosphazene ring is protonated. As a result four nitrate anions are required to compensate the charge and three of these are chelating the Dy(III) center while one is a monodentate ligand of the Cu(II) site. None of the nitrate ligands are involved in a bridging coordination mode.

The CuI coordination sphere adopts a distorted square pyramidal geometry (2N, 3O) (Supporting Information) similar to that found in 4. On the other hand, the Dy(III) coordination sphere is totally different of the one observed for the calcium site in 4. In 6, Dy(III) displays a rare 10-fold coordination (10 O) (Supporting Information) with six of the oxygen atoms from the nitrate anions while four are brought by the hydrazone ligand. Interestingly, among the three nitrate ligands that bind to Dy(III), two are anisobidentate while one is isobidentate (O4 and O5) (Supporting Information, Table S18). Cu(II) and Dy(III) in this heterobimetallic complex are bound to each other by the bridging phenoxido oxygen atoms O16 and O15. The resulting CuDyO₂ four-membered ring is planar. In the carbophosphazene part, the C–N bond distances C1–N2 1.381(8) and C2–N2 1.405(8) Å are lengthened in comparison to C1–N3 1.339(9) and C2–N1 1.323(8) Å as a result of N2 protonation. However, the carbophosphazene ring remains quasi-planar (Supporting Information).

The coordination ability of the carbophosphazene ligand 2 and the cyclophosphazene ligand 3 is very similar as illustrated experimentally by the isolation and the structural characterization of the 3d-4f heterobimetallic complexes [{NP(O₂C₁₂H₈)₂}{NP{N(CH₃)N=CH-C₆H₃-(*o*-O)(*m*-OCH₃)₂}}{CuDy(NO₃)₃}] (7) (Figure 4) and [{NP(O₂C₁₂H₈)₂}{NP{N(CH₃)N=CH-C₆H₃-(*o*-O)(*m*-OCH₃)₂}}{CuTb(NO₃)₃}] (8) (Supporting Information, Figure S3). The cyclophosphazene ring that is nonplanar in 7 and 8 (Supporting Information) supports an identical coordination platform as that of the carbophosphazene ligand. Dy(III) and Tb(III) metal ions in these complexes, exhibit an identical ten-coordinate coordination sphere with only oxygen atoms from three chelating nitrate anions and the hydrazone ligand (Supporting Information). In both 7 and 8, the five-coordinate Cu(II) site adopts a nearly square pyramidal geometry (2O, 3N). Like in the previous compounds, the Cu(II) and the

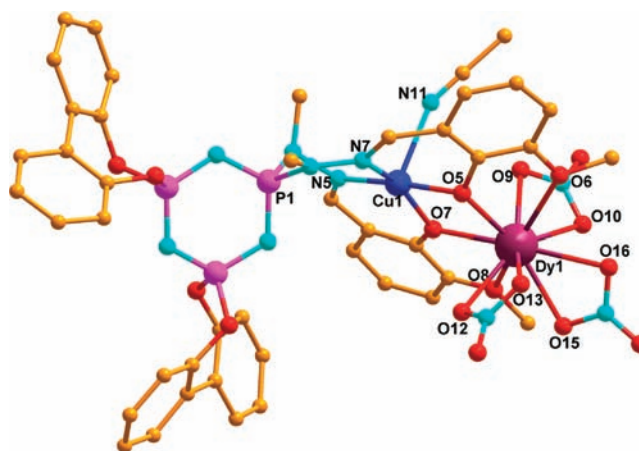


Figure 4. Molecular structure of 7.

lanthanide metal ion are bridged by the phenoxide oxygen atoms. The bond distances found in 7 and 8 are similar and typical of those found in these systems and the other described complexes. Selected bond distances and angles of these compounds are summarized in Supporting Information, Tables S19 and S20.

Magnetic Properties. At room temperature, the χT product for 6, 7, and 8 (Figure 5) is 14.8, 14.4, and 13.9 cm³

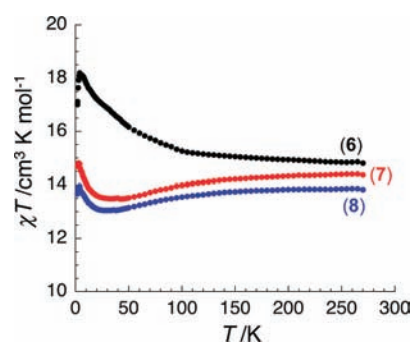


Figure 5. χT vs T data for 6, 7, and 8 at 1000 Oe (with χ defined as the magnetic susceptibility and equal to M/H per complex).

K/mol, respectively, in very good agreement with the expected values of 14.545 and 12.19 cm³ K/mol for one $S = 1/2$ Cu(II) (with a g factor slightly higher than 2) and one Dy(III) metal ions ($S = 5/2$, $L = 5$, ${}^6H_{15/2}$ $g = 4/3$; $C = 14.17$ cm³ K/mol) for 6 and 7 or for one Tb(III) metal ions ($S = 3$, $L = 3$, 7F_6 $g = 3/2$; $C = 11.815$ cm³ K/mol) for 8. When the temperature is lowered, the χT product for 6 increases slowly reaching a maximum around 3 K at 18.2 cm³ K/mol. At lower temperatures, the χT product at 1000 Oe decreases significantly to a minimum value at 1.8 K of 17 cm³ K/mol. This thermal behavior indicates the presence of ferromagnetic interaction between Dy(III) and Cu(II) spin carriers as already observed in these types of complexes.¹⁷ The decrease of the χT product below 3 K is certainly due to the presence of magnetic anisotropy and/or intercomplex magnetic interactions.

On the other hand, the thermal behavior of 7 and 8 is quite different. When the temperature is lowered, the χT product is slowly decreasing reaching a minimum in both cases around 33 K at 13.5 and 13.0 cm³ K/mol for 7 and 8, respectively. At lower temperature, the χT product at 1000 Oe increases significantly to reach respectively 14.8 and 14.0 cm³ K/mol at 3

K for **7** and **8**, respectively. At lower temperatures, a tiny decrease of the χT product is observed to 14.7 and 13.7 cm³ K/mol at 1.8 K. Even if the global thermal behavior seems to be different from **6**, these data support again the presence of ferromagnetic interaction between Dy(III) and Cu(II) spin carriers as already observed in this type complex but also in **6**. The only difference in **7** and **8** is the magnitude of the ferromagnetic coupling that seems to be weaker than in **6**, and thus the thermal depopulation of the Dy^{III} or Tb^{III} excited states (Stark sublevels of the ⁶H_{15/2} or ⁷F₆ state), that induces a decrease of the χT product between 300 and 30 K, is dominating the high temperature behavior of these compounds.¹⁸ The decrease of the Cu–Dy ferromagnetic interaction between **6** and **7** is certainly due to the slight change of the geometry around the Cu(II) metal ions and the bridging Dy–(O)₂–Cu motif. Again in these two compounds, the decrease of the χT product below 3 K is certainly due to the presence of magnetic anisotropy and/or intercomplex magnetic interactions. The field dependence of the magnetization below 8 K (Supporting Information, Figures S6–S8) reveals a relative rapid increase of the magnetization at low fields without inflection point or “S” shape curve that confirms the ferromagnetic nature of the magnetic interactions in these compounds. At high temperature, the magnetization increases slowly and linearly without a clear saturation even at 2 K under 7 T at which it reaches 7.7, 6.9, and 6.6 μ_B for **6**, **7**, and **8** respectively. This high field variation of the magnetization suggests the presence of a significant magnetic anisotropy or low lying excited states that is also confirmed by the *M* versus *H/T* plots (Supporting Information, Figures S6–S8, that is, the data are not all superposed on a single master-curve further). In addition, it is worth noting that no hysteresis on the *M* versus *H* data has been observed above 1.8 K with sweep-rate used in a traditional SQUID magnetometer (100–200 Oe/min). Accordingly, ac susceptibility measurements on these compounds in zero dc field revealed a total absence of out-of-phase signal and thus slow relaxation of the magnetization.

CONCLUSION

Cyclocarbophosphazene and cyclophosphazene bishydrazides [N C (N M e₂)]₂ [N P { N (C H₃) - N H₂ }₂]₂ a n d { N₃P₃(O₂C₁₂H₈)₂[N(Me)NH₂]₂ } are excellent precursors that can be elaborated readily into dual-pocket multisite coordination hydrazone ligands. In accordance with their design these ligands readily afford heterometallic derivatives where the inner coordination pocket binds to the transition metal ion while the outer pocket coordinates to Ca²⁺ or Ln³⁺. Magnetic studies on the new 3d-4f systems (Cu²⁺/Dy³⁺) or Cu²⁺/Tb³⁺) reveals that these possess weak intracomplex magnetic interactions and significant magnetic anisotropy. However, we were unable to detect any out-of-phase signal in the ac susceptibility studies thus ruling out the existence of slow relaxation of magnetization in these systems above 1.8 K.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. Further details are given in Figures S1–S8 and Tables S1–S21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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DEDICATION

[#]This paper is dedicated to Prof. G. R. Desiraju on the occasion of his 60th birthday.

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