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Synthesis of Zigzag-Chain and Cyclic-Octanuclear Calcium Complexes and Hexanuclear Bulky Aryl-Phosphate Sodium Complexes with Ortho-Amide Groups: Structural Transformation Involving a Network of Inter- and Intramolecular Hydrogen Bonds

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Abstract: Three new polynuclear Ca(II)- and Na(I) phosphate complexes with two strategically oriented bulky amide groups, $2,6\text{-}(PhCONH)_2C_6H_3OPO_3H_2$, were synthesized, including one with a zigzag-chain, $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}(H_2O)_4(EtOH)]_n$, a cyclic-octanuclear form, $[Ca^{II}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8\text{-}(O{=}CHNMe_2)_8(H_2O)_{12}]$, and a hexanuclear complex, $(NHEt_3)[Na_3\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_2(H_2O)\text{-}(MeOH)_7]$. X-ray crystallography revealed that all have an *unsymmetric* ligand position due to the bulky amide groups. A dynamic transformation of the Ca(II) zigzag-chain structure to the cyclic-octanuclear complex was induced by changing coordination of DMF molecules, which caused a reorganization of the intermolecular/intramolecular hydrogen bond network.

Introduction

The structural polynuclear phosphate complexes with various metal ions and hydrogen-bond donor ligands provide fascinating insight for the design of solid-state materials. Ca(II) phosphate complexes are of special interest for their relevance to biological issues, and their structure in particular may yield clues for understanding the biomineralization of Ca(II) phosphate materials, such as bone and teeth.[1−6] It has been reported that synthetic metal−phosphate complexes with small ligands have open-framework structures,[7−20] in which intermolecular hydrogen-bond networks play an important role for developing a variety of metal−phosphate complexes.[21−30] Similar structures have important applications for ion exchange and catalysis.

We have previously synthesized novel mononuclear Ca(II) phosphate complexes with an extremely bulky amide ligand,[31] whose mononuclear structure enabled us to investigate the role of intramolecular NH···O hydrogen bonds to the phosphate groups, because the bulky ligand interrupts the formation of intermolecular hydrogen-bond interactions. The bulky triphenylacylamino groups lead to the formation of a mononuclear Ca(II) core in both the phosphate monoanion and dianion states.

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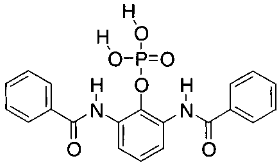
Scheme 1. Novel Aryl Dihydrogen Phosphate Ligand with Bulky Amide Substituents in Ortho Positions



1

The intramolecular NH···O hydrogen bonds to the phosphate groups, which are not formed in a phosphoric acid state, are weak in a monoanion state and strong in a dianion state. The NH···O hydrogen bonds to the coordinating phosphate groups prevent the Ca−O bond from dissociating. The correlation study between the distance of a Ca−O bond and the angles of a Ca−O−P among various Ca(II) phosphate complexes showed the presence of the covalent bond character in the Ca−O bonds. In fact the analysis for our mononuclear Ca(II) complex gives the shortest Ca−O bond. The very bulky amide group seemed to restrict the coordination of the phosphate groups to the Ca(II) ion and the formation of intermolecular hydrogen-bond networks.

It is known that the various Ca(II) complexes with phosphate, $ROPO_3$, and phosphonate ligands, RPO_3, such as $Ca(O_3POCH_2CH_2NH_3)$, have a one-dimensional structure[32−35] and the others, such as $Ca(O_3PMe)$, have layered structures,[36−39] whereas Na phosphate complexes are reported to be polymeric as well.[40−42] In this present work, we show our synthetic novel phosphate ligands with bulky benzoylamino groups in ortho positions (Scheme 1), zigzag-chain, cyclic-octanuclear Ca(II) and hexanuclear Na(I) complexes forming intramolecular and intermolecular hydrogen-bond networks. These phosphate complexes give a unique *unsymmetric* ligand position to the metal ions. We present a report of their isolation method and characterization by X-ray studies and by NMR and IR spectra.

Experimental Section

Materials. All solvents were distilled over appropriate drying agents and degassed prior to use. All starting reagents were of commercial grade. 2,6-Dibenzoylaminophenyl dihydrogen phosphate was synthesized by the reported methods.[43]

2,6-$(PhCONH)_2C_6H_3OH$. A suspension of 970 mg (4.9 mmol) of 2,6-$(NH_2)C_6H_3OH\cdot 2HCl$ was prepared in 130 mL of dichloromethane. To the suspension, 3.6 mL (26 mmol) of triethylamine and 1.8 mL (19 mmol) of benzoyl chloride were added at 0 °C under Ar atmosphere. After being stirred for a few hours, the solution was brought to room temperature with additional stirring. After the addition of water, the solution was concentrated in vacuo to give a white precipitate, which was a benzoyl ester of the final product. The ester was hydrolyzed in 1 M NaOH aqueous methanol (1:1). The solution was neutralized with concentrated aqueous HCl and concentrated in vacuo. The residue was extracted with portions of 100 mL of ether, and the separated organic layer was washed with saturated aqueous NaCl solution, dried over Na_2SO_4, and concentrated in vacuo to give a pale-yellow powder. Yield, 80%. ^1H NMR ($CDCl_3$): δ 9.94 (s, 2H, OH), 8.54 (s, 2H, NH), 7.95 (d ($J = 7.14$ Hz), 4H, *m*-PhH), 7.63 (d ($J = 8.06$ Hz), 2H, *m*-ArH), 7.60 (t ($J = 7.14$ Hz), 2H, *p*-PhH), 7.53(d ($J = 7.55$ Hz), 4H, *m*-PhH), 6.98 (t ($J = 8.06$ Hz), 1H, *p*-ArH). Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.10; H,4.79; N, 8.42.

2,6-$(PhCONH)_2C_6H_3OPO_3H_2$ (1). To a suspension of 2,6-$(PhCONH)_2C_6H_3OH$ (1.7 g, 5.2 mmol) in 60 mL of acetonitrile were added orthophosphoric acid (1.2 g, 12 mmol), triethylamine (3.3 mL, 22 mmol), and trichloroacetonitrile (3.1 mL, 31 mmol) to give a homogeneous green solution. This solution was stirred for 5 h at room temperature and concentrated under reduced pressure. To the residue was added 50 mL of water, and the aqueous phase was washed with ether a few times to remove the unreacted phenol. The aqueous phase was adjusted to pH 8 with 1 M NaOH aqueous solution and concentrated in vacuo to remove triethylamine. The concentrated solution was acidified with concentrated HCl. Colorless needles precipitated in 1 week. Yield, 19%. ^1H NMR (DMSO-d_6): δ 10.13 (s, 2H, NH), 8.00 (d ($J = 8.25$ Hz), 4H, *m*-PhH), 7.95 (d ($J = 8.06$ Hz), 2H, *m*-ArH), 7.60 (t ($J = 7.14$ Hz), 2H, *p*-PhH), 7.53(d ($J = 7.11$ Hz), 4H, *m*-PhH), 7.21 (t ($J = 8.06$ Hz), 1H, *p*-ArH). MS (ESI) Calcd (found) *m/e*: 2,6-$(PhCONH)_2C_6H_3OPO_3H^-$, 411.3 (411.6). ^{31}P NMR (DMSO-d_6): δ −1.13 ppm. ^{31}P NMR (in the solid state): δ −6.6 ppm. Anal. Calcd for $C_{20}H_{17}N_2O_6P\cdot(H_2O)_{0.5}$: C, 57.01; H, 4.31; N, 6.65. Found: C, 56.77; H, 4.32; N, 6.53. pK_{a1} and pK_{a2} values: 4.3 and 7.1 in 5 mM Triton X-100/10% aqueous micellar solution.

$(NHEt_3)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (2a). To a suspension of 2,6-$(PhCONH)_2C_6H_3OH$ (550 mg, 1.7 mmol) in 30 mL of acetonitrile were added orthophosphoric acid (380 g, 3.9 mmol), triethylamine (1.1 mL, 7.8 mmol), and trichloroacetonitrile (1.0 mL, 10 mmol) to give a homogeneous green solution. This solution was stirred for 5 h at room temperature. To the residue was added 10 mL of water, and the aqueous phase was washed with ether a few times to remove the unreacted phenol. Acidification of the solution gave a white precipitate, which was recrystallized from acetonitrile. Yield 46%. Anal. Calcd for $C_{26}H_{32}N_3O_6P_1$: C, 60.81; H, 6.28; N, 8.18. Found: C,60.81; H,6.23; N,8.24.

$(NEt_4)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (2b). To a solution of 100 mg (0.24 mmol) of 2,6-$(PhCONH)_2C_6H_3OPO_3H_2$ in 3 mL of methanol was added 63 mg (0.24 mmol) of $(NEt_4)(OAc)$ in 3 mL of aqueous methanol, and the solution was concentrated under reduced pressure. The residue was recrystallized from acetonitrile−ether to give colorless crystals. Yield, 71%. Anal. Calcd for $C_{28}H_{36}N_3O_6P_1$: C, 62.10; H, 6.70; N, 7.76. Found: C, 62.17; H, 6.67; N, 7.83.

$[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}(H_2O)_4(EtOH)]_n$ (3). To a solution of **1** (68 mg, 0.16 mmol) in 2 mL of MeOH was added an aqueous solution of $Ca(OAc)_2\cdot H_2O$ (28 mg, 0.16 mmol) in 1 mL of water. The solution was concentrated in vacuo, and the residue was recrystallized from ethanol to give colorless crystals. Yield, 25%. Anal. Calcd for $C_{20}H_{15}CaN_2O_6P_1\cdot(H_2O)_4$: C, 45.98; H, 4.44; N, 5.36. Found: C, 45.54; H, 4.69; N, 5.19. This compound was confirmed by X-ray structure determination.

$[Ca^{II}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$ (4). **3** was recrystallized from DMF/ether to precipitate colorless crystals. Anal. Calcd for $C_{184}H_{200}Ca_8N_{24}O_{68}P_8\cdot(DMF)_4(H_2O)_{18}$: C, 47.06; H, 5.28; N, 7.84. Found: C, 47.07; H, 5.08; N, 7.79. This compound was confirmed by X-ray structure determination.

$(NHEt_3)[Na_3\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_2(H_2O)(MeOH)_7]$ (5). $(NHEt_3)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (752 mg, 1.46 mmol) was dissolved in 5 mL of MeOH, and 1.5 equiv of aqueous NaOH solution was added. The solution was concentrated, and the residue was recrystallized from MeOH/ether. Yield 35%. Anal. Calcd for $C_{46}H_{45}N_5$-

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Table 1. Crystallographic Data for **2a**, **2b**, **3**, **4** and **5**

parameter	**2a**	**2b**	**3**	**4**·$(DMF)_8(H_2O)_{11}$	**5**
empirical formula	$C_{26}H_{32}O_6N_3P$	$C_{28}H_{36}N_3O_6P$	$C_{22}H_{29}CaN_2O_{11}P$	$C_{208}H_{278}Ca_8N_{32}O_{87}P_8$	$C_{53}H_{76}N_5Na_3O_{20}P_2$
formula weight	513.53	541.57	568.52	5187.02	1234.1
color	colorless	colorless	colorless	colorless	colorless
crystal system	triclinic	orthorombic	monoclinic	tetragonal	triclinic
lattice parameter					
a, Å	11.910(3)	18.678(6)	16.960(5)	29.8134(5)	15.1649(13)
b, Å	14.612(3)	31.752(11)	8.257(7)	29.8134(5)	16.8922(16)
c, Å	8.142(1)	9.380(6)	18.754(7)	16.9925(3)	14.3956(10)
α, deg	100.79(2)	90	90	90	114.6090(10)
β, deg	108.64(1)	90	101.95(3)	90	109.742(5)
γ, deg	78.99(2)	90	90	90	71.321(2)
V, Å^3	1305.6(5)	5563(4)	2569(2)	15103.6(4)	3085.4(4)
space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)	$P2_1/n$ (no. 14)	$P4/n$ (no. 85)	$P\bar{1}$ (no. 2)
Z	2	8	4	2	2
ρ_{calc}, g cm^{-1}	1.306	1.293	1.470	1.141	1.328
μ (Mo Kα), cm^{-1}	1.50	1.45	3.68	2.60	1.67
temp (K)	296	296	296	296	173
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	ω	ω
$2\theta_{max}$, deg	50.0	55.0	50.0	55.0	55.0
no. of collected reflns	4844	5806	3662	17887	21113
no. of unique reflens	4600	5132	3231	17290	13273
no. of reflns used	2170	5132	3231	17290	13267
	($I > 2\sigma(I)$)	(all)	(all)	(all)	(all)
no. of variables	325	344	338	631	749
R1^a	0.062 (R^c)	0.053	0.052	0.105	0.072
wR2^b	0.067 ($R_w{}^d$)	0.248	0.181	0.340	0.211

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $[I > 2\sigma(I)]$. [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

$Na_3O_{15}P_2$·$(H_2O)_5(MeOH)$: C, 48.63; H, 5.12; N, 6.03. Found: C, 48.74; H, 5.20; N, 6.16. MS (ESI) Calcd (found) *m*/*e*: $[Na_3\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3\}_2 + 2\ H^+]^+$, 891.2 (891.6). ^{23}Na NMR (DMSO-d_6): δ 0.54 ppm. ^{23}Na MAS NMR (in the solid state): δ −11.4 ppm.

Physical Measurement. ^{1}H NMR spectra in solution were recorded on a JEOL EX 400 spectrometer. ^{31}P and ^{23}Na NMR and spectra in solution were recorded on a Varian Unity Plus 600 MHz spectrometer. ^{31}P, ^{23}Na NMR, and CRAMPS (combined rotation and multipulse spectroscopy) ^{1}H NMR spectra in the solid state were recorded on a Chemmagnetics CMX-300. CRAMPS ^{1}H NMR spectra in the solid state were taken with a 4 mm ϕ pencil rotor cell using an MREV-8 pulse sequence.[44] IR spectra in the solid state of KBr pellets were taken on a Jasco FT/IR-8300 spectrometer. The pK_a measurement was performed on a Metrohm 716 DMS Titrino. The pK_a value for **1** was measured in a 10% DMF−90% aqueous micellar (Triton X-100 micelles) solution. Mass spectroscopic analysis was performed on a PE-Sciex API-III plus and Finniganmat LCQ-MS instrument.

X-ray Crsytal Structure Determination. The following crystals of $(NHEt_3)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (**2a**), $(NEt_4)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}\}$ (**2b**), $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\{H_2O)_4(EtOH)]_n$ (**3**), $[Ca^{II}{}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$ (**4**), and $(NHEt_3)[Na_3\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_2(H_2O)(MeOH)_7]$ (**5**) were sealed in glass capillaries. The X-ray data for **2a**, **2b**, and **3** were collected at 23 °C on a Rigaku AFC5R and an AFC7R diffractometer equipped with a rotating anode X-ray generator. The radiation used was Mo Kα monochromatized with graphite (0.71069 Å). No empirical absorption correction was applied. Unit cell dimensions were refined by 20 reflections. These standard reflections were monitored with every 150 reflections and did not show any significant change. The X-ray data for **4** and **5** were collected in 4.0 and 5.0° oscillations at 296 and 173 K on a Raxis RAPID, respectively. Sweeps of data for **4** and **5** was done using ω oscillations from 130.0 to 190.0° at $\phi = 0.0°$ and $\chi = 45.0°$, and from 0.0 to 160.0° at $\phi = 180.0°$ and $\chi = 45.0°$. The basic crystallographic parameters for **2a, 2b**, **3**, **4**, and **5** are listed in Table 1.

The structures were solved by the direct method and expanded using Fourier techniques using a *teXsan* crystallographic software[45] and SHELXL-97.[46] Non-hydrogen atoms were refined anisotropically, but the hydrogen atoms were refined isotropically in **2a**, **2b**, **3**, and **5**. Solvent molecules for **4** were refined isotropically, and all H atoms except water H atoms were located at the calculated positions.

Results and Discussion

Crystal Structures. Figure 1 represents the molecular structures of $(NHEt_3)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (**2a**), and $(NEt_4)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ **(2b)**. The P−O distances for **2a**, 1.502 (P1−O11), 1.491 (P1−O12), 1.549 Å (P1−O13), indicate that O13 is protonated to give a P−O(H) single bond, and the anionic charge due to the other oxygen atom is delocalized over the other two P−O bonds. The distance of N1−O11 (3.002(6) Å), N2−O12 (2.744(6) Å) for **2a** and that of N1−O12 (2.739(7) Å), N2−O13 (3.227(7) Å) are in a range of forming NH···O hydrogen bonds. The short O−O distance (2.531(5) Å for **2a** 2.528(6) Å for **2b**) between O13 and O11 of the neighboring ligand indicates the formation of the P−OH···O−P hydrogen bonds between the two ligands in the phosphate monoanion state to construct the dimer unit structures.

The molecular structure of a phosphate dianion complex, $[Ca\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2(H_2O)_4(EtOH)]_n$ (**3**), is shown in Figure 2a, and the selected bond distances and bond angles for **3** are listed in Table 2. The Ca(II) center is a seven-coordinate structure in a capped-octahedral geometry. Four oxygen atoms of water molecules, O21, O22, O23, and O24, coordinate to Ca(II), and O31 of the ethanol is in the capping position. The bond lengths, Ca1−O11 and Ca1−O13, are 2.427(4) Å and 2.326(5) Å, respectively which are within the normal range.[37]

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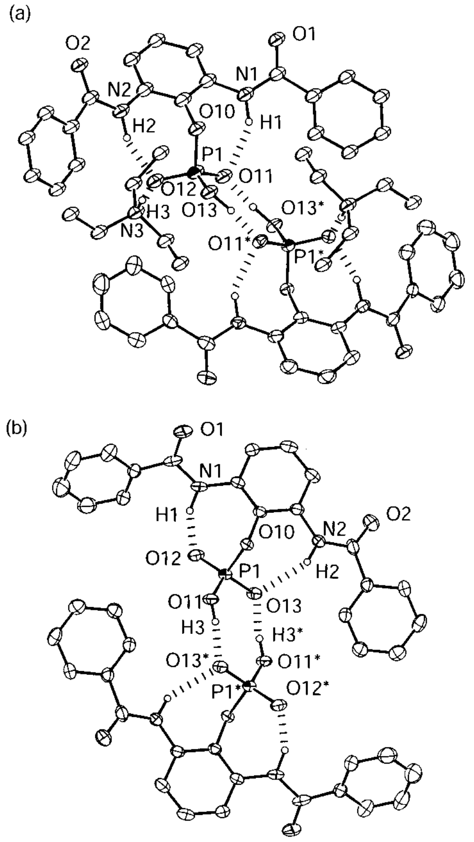

Figure 1. Molecular structure of (a) $(NHEt_3)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (**2a**) and (b) $(NEt_4)\{2,6\text{-}(PhCONH)_2C_6H_3OPO_3H\}$ (**2b**). A dashed line indicates a hydrogen bonds.

Table 2. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg) for **3**

Bond Distances			
Ca(1)−O(11)	2.427(4)	Ca(1)···Ca(1)*	5.538(2)
Ca(1)−O(13)	2.326(5)		
P(1)−O(10)	1.654(4)	P(1)−O(11)	1.515(5)
P(1)−O(12)	1.529(5)	P(1)−O(13)	1.510(5)
N(1)···O(11)	3.149(6)	N(2)···O(12)	2.866(7)
Bond Angles			
Ca(1)−O(11)−P(1)	124.8(2)	Ca(1)−O(13)−P(1)	137.1(3)
O(10)−P(1)−O(11)	107.1(2)	O(10)−P(1)−O(12)	104.9(2)
O(10)−P(1)−O(13)	101.5(2)	O(11)−P(1)−O(12)	114.2(3)
O(11)−P(1)−O(13)	113.5(3)	O(12)−P(1)−O(13)	114.2(3)
N(1)−H(1)···O(11)	147.34	N(2)−H(2)···O(12)	151.01
Torsion Angles			
C(17)−N(1)−C(12)−C(11)	145.3(7)	C(18)−N(2)−C(16)−C(11)	−143.9(7)

The phosphate dianion ligands bridge between two Ca(II) ions with bond angles of Ca1−O11−P1 and Ca1−O13−P1 as 124.8(2)° and 137.1(3)°, respectively.

The phosphate dianion ligands coordinate to Ca(II) ions in a bridging-bidentate mode, and the unit forms an infinite zigzag-chain structure. Figure 2 (parts b and c) represents a view from above the *yz* and *xz* plane, respectively, of the one-dimensional zigzag structure of **3**. The ligand is aligned alternatively along the Ca axis (*y* axis). The short Ca···Ca distance is 5.538(2) Å, and the longer Ca···Ca distance in the same stem is 8.257(7) Å. Each zigzag chain is covered by the bulky benzoylamino groups and gives a tubular ligand alley. The distances between the oxygen atoms of amide carbonyl and the water molecule coordinated to a Ca(II) ion, O1−O23 and O2−O24, are 2.858(6) and 2.765(9) Å, respectively. These distances imply that these oxygen atoms are in van der Waals contact with each other. Each zigzag Ca(II) chain is stacked by intermolecular

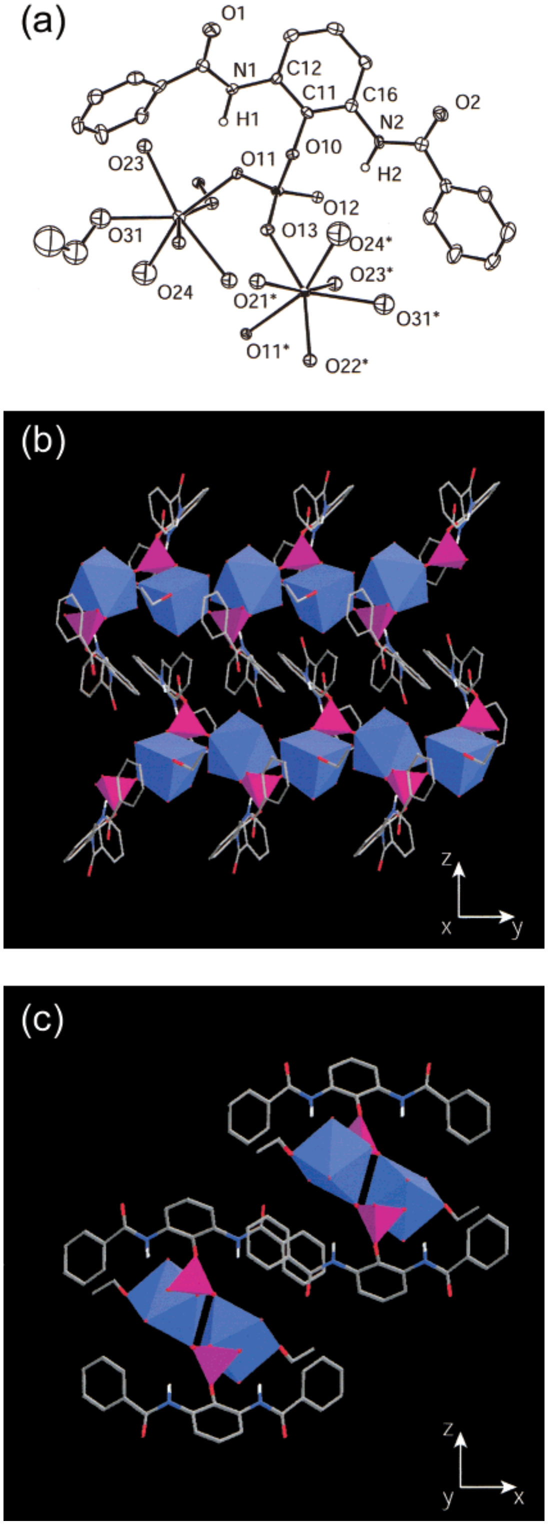

Figure 2. (a) Unit structure of $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}(H_2O)_4\text{-}(EtOH)]_n$ (**3**). View of the chain structure of $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}(H_2O)_4(EtOH)]_n$ (**3**) from (b) above the *yz* plane and (c) above the *xz* plane (a top view). Ca(II) coordination spheres and the phosphate groups are presented as blue and pink polyhedrons, respectively. Hydrogen atoms except for amide NH protons are omitted for clarity.

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for **4**

Bond Distances			
Ca(1)···Ca(2)	3.705(2)	Ca(1)···Ca(1)*	6.020(2)
Ca(1)···Ca(2)*	3.721(2)	Ca(1)···Ca(1)**	8.513(2)
Ca(1)−O(12)	2.499(5)	Ca(1)−O(13)	2.506(4)
Ca(1)−O(22)	2.356(4)	Ca(1)−O(23)	2.367(4)
Ca(2)−O(12)	2.369(4)	Ca(2)−O(13)	2.364(4)
Ca(2)−O(22)	2.519(4)	Ca(2)−O(23)	2.499(5)
Ca(1)−O(31)	2.325(5)	Ca(2)−O(41)	2.296(5)
P(1)−O(10)	1.647(4)	P(1)−O(11)	1.501(5)
P(1)−O(12)	1.510(4)	P(1)−O(13)	1.521(4)
P(2)−O(20)	1.646(4)	P(2)−O(21)	1.507(5)
P(2)−O(22)	1.510(4)	P(2)−O(23)	1.512(4)
N(1)···O(12)	3.178(8)	N(2)···O(11)	2.869)8)
N(3)···O(21)	2.883(9)	N(4)···O(22)	3.195(6)
Bond Angles			
Ca(1)−O(12)−P(1)	95.9(2)	Ca(1)−O(13)−P(1)	95.3(2)
Ca(1)−O(22)−P(2)	138.5(2)	Ca(1)−O(23)−P(2)	141.4(3)
Ca(2)−O(12)−P(1)	140.7(3)	Ca(2)−O(13)−P(1)	140.0(2)
Ca(2)−O(22)−P(2)	95.51(19)	Ca(2)−O(23)−P(2)	96.3(2)
O(10)−P(1)−O(11)	107.4(3)	O(10)−P(1)−O(12)	104.3(2)
O(10)−P(1)−O(13)	102.5(2)	O(11)−P(1)−O(12)	115.8(3)
O(11)−P(1)−O(13)	115.8(3)	O(12)−P(1)−O(13)	109.4(3)
O(20)−P(2)−O(21)	107.4(3)	O(20)−P(2)−O(22)	105.0(2)
O(20)−P(2)−O(23)	102.2(2)	O(21)−P(2)−O(22)	115.2(3)
O(21)−P(2)−O(23)	116.2(2)	O(22)−P(2)−O(23)	109.3(3)
N(1)−H(1)···O(12)	142.13	N(2)−H(2)···O(11)	137.56
N(3)−H(3)···O(21)	143.53	N(4)−H(4)···O(22)	146.11
Torsion Angles			
C(17)−N(1)−C(12)−C(11)	144.8(7)	C(18)−N(2)−C(16)−C(11)	−121.9(8)

OH···O=C hydrogen bonds with the amide groups to give an *anti* parallel alignment.

A recrystallization of **3** in the presence of DMF gives an octanuclear Ca(II) complex with DMF coordination, $[\mathrm{Ca^{II}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}}]$ (**4**). Figure 3a shows a unit structure for **4,** and its selected bond distances and bond angles are listed in Table 3. All of the Ca(II) ions have a seven-coordinate structure in pentagonal-bipyramidal geometry. Four oxygen atoms of the neighboring phosphate ligand and one water molecule coordinate in equatorial positions. O31, an amide oxygen of DMF, and O32, an oxygen atom of a water molecule, exist at each one of the axial positions. The Ca1−O31 distance (2.325(5) Å) is in the range of the normal reported distances (2.25−2.34 Å).[47−54] The two oxygen atoms (O12 and O13) of the coordinating ligand are in a monodentate-bridging mode to two Ca(II) ions: O12 coordinates to Ca1 and Ca2*, and O13 to Ca1 and Ca2. Each of the phosphate ligands binds to three Ca(II) ions. Ca1 is coordinated with both O12 and O13 (ca 2.50 Å) in a *syn* position (Ca−O−P ≈ 95°). The other two Ca(II) ions, Ca2 and Ca2*, which have shorter Ca−O distances (2.369(4) and 2.364(4) Å, respectively), lie in the *anti* positions (Ca−O−P is av 144.4°).

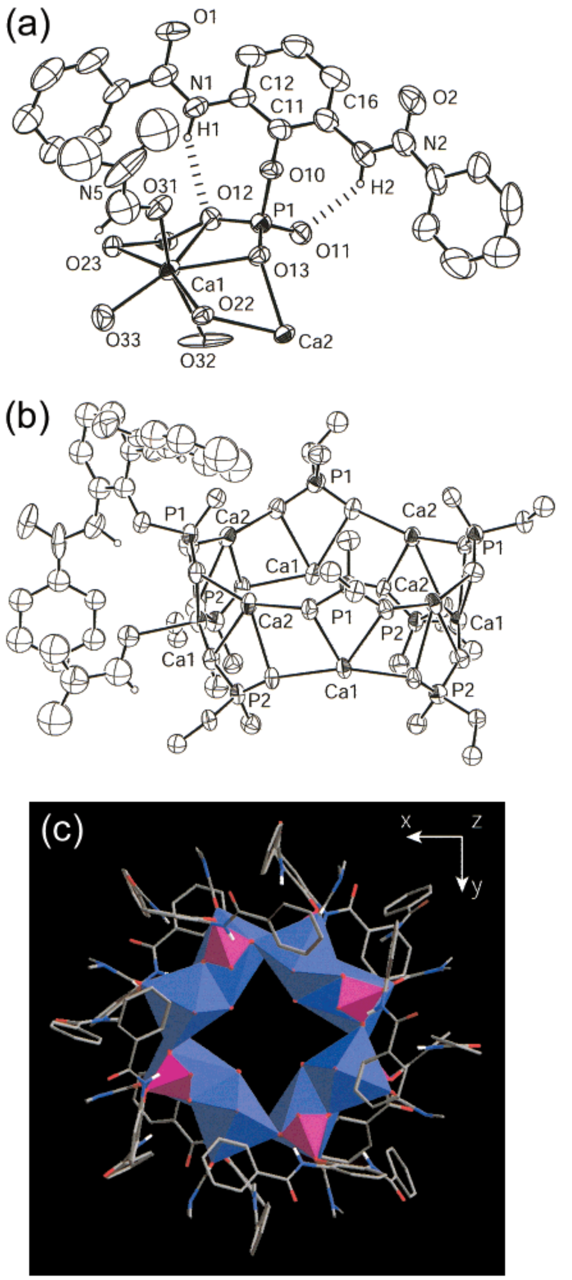

Figure 3. (a) Unit structure containing Ca1 of $[\mathrm{Ca^{II}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}}]$ (**4**) and (b) an inner view of the repeated units of the cyclic-octanuclear Ca(II) structure of **4** with only one of the ligands together with a DMF molecule. (c) Whole molecular structure. Ca(II) coordination spheres and the phosphate groups in (c) are presented as purple and pink polyhedrons, respectively.

Figure 3b shows the octanuclear Ca(II) cluster alternately coordinated by one of the phosphate oxygen atoms and a DMF. The octanuclear Ca(II) core has a C_4 symmetry and has two crystallographically nonequivalent Ca(II) ions (Ca1 and Ca2). This repeated Ca(II) coordination gives a cyclic-octanuclear structure consisting of a Ca−O−Ca−O diamond core. It has been reported that a similar diamond chain structure repeats infinitely due to the planarity of the Ca−O−Ca−O plane,[34,35,39] although the plane for **4** is folded by 53° on the O−O axis. Here, our phosphate ligands and DMF molecules cover the cyclic Ca ion alley. The units consisting of the Ca(II) ion and the phosphate ligand are alternatively aligned to form an eight-membered crown structure including four Ca(II) ions both at

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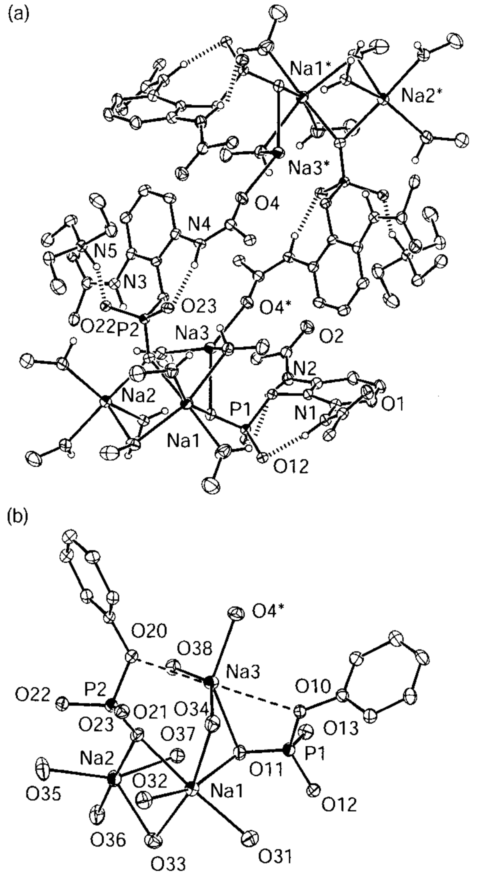

Figure 4. (a) Whole molecular structure and (b) core structure of $(\mathrm{NHEt_3})[\mathrm{Na_3}\{\mathrm{O_3POC_6H_3}\text{-2,6-}(\mathrm{NHCOPh})_2\}_2(\mathrm{H_2O})(\mathrm{MeOH})_7]$ (**5**).

the top and at the bottom (Figure 3c). The diameter of its ring is 8.513(2) Å, which forms the longest Ca···Ca (opposite) separation. Eight water molecules coordinating to each of the Ca(II) ions exist inside the Ca(II) cluster ring.

Figure 4 shows the hexanuclear structure with a trinuclear core of $(\mathrm{NHEt_3})[\mathrm{Na_3}\{\mathrm{O_3POC_6H_3}\text{-2,6-}(\mathrm{NHCOPh})_2\}_2(\mathrm{H_2O})(\mathrm{MeOH})_7]$ (**5**). A trinuclear core consists of two phosphate dianion ligands, three Na ions and one $\mathrm{NHEt_3}^+$ cation. The distances of Na1···Na2 and Na1···Na3 are 3.326(2) and 3.337(2) Å, respectively (see Table 4). Oxygen atoms from a phosphate dianion ligand and from methanol coordinate to the Na ions in μ_2 fashion to form a diamond core. The Na1 ion has an octahedral geometry, but the Na2 ion forms a distorted trigonal bipyramidal structure simply because the steric repulsion of the phenyl ring occurs near the Na2 ion. A Na3 ion is ligated with O11, O34, O38, and O4 in the neighboring trinuclear core with a distorted tetrahedral geometry and is also weakly coordinated with O20 and O10. The coordination of the amide carbonyl oxygen, O4*, results in the dimerization of the trinuclear structure.

The two uncoordinated oxygen atoms, O12 and O13, are hydrogen-bonded with amide NH groups. In the other ligands, the uncoordinated phosphate O22 and O23 atoms are hydrogen-bonded from ammonium N5H5 and amide N4H4, respectively. A remarkable point for the coordination geometry for the phosphate dianion complex **5** is that the negative charge (−1) of the dianion ligands are compensated for with the double NH···O hydrogen bonds from the amide or the ammonium NHs.

Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for **5**

Bond Distances			
Na(1)···Na(2)	3.326(2)	Na(1)···Na(3)	3.337(2)
Na(2)···Na(3)	4.458(2)		
P(1)−O(10)	1.649(2)	P(1)−O(11)	1.503(2)
P(1)−O(12)	1.522(2)	P(1)−O(13)	1.501(2)
P(2)−O(20)	1.661(2)	P(2)−O(21)	1.501(2)
P(2)−O(22)	1.515(2)	P(2)−O(23)	1.524(3)
Na(1)−O(11)	2.407(3)	Na(1)−O(21)	2.384(3)
Na(3)−O(4)	2.325(3)	Na(3)−O(11)	2.457(3)
Na(3)−O(20)	2.617(3)	Na(3)−O(34)	2.463(3)
Na(3)−O(38)	2.516(3)		
N(1)···O(12)	2.888(3)	N(2)···O(13)	2.915(3)
N(3)···O(22)	3.461(4)	N(4)···O(23)	2.876(3)
Bond Angles			
O(11)−Na(1)−O(21)	87.02(9)	O(11)−Na(1)−O(31)	84.44(10)
O(11)−Na(1)−O(32)	159.85(10)	O(11)−Na(1)−O(33)	100.01(9)
O(11)−Na(1)−O(34)	82.63(9)	O(11)−Na(3)−O(34)	82.93(9)
O(11)−Na(3)−O(38)	90.05(9)	O(21)−Na(2)−O(33)	92.26(10)
O(21)−Na(2)−O(35)	88.71(10)	O(21)−Na(2)−O(36)	170.99(12)
O(21)−Na(2)−O(37)	87.09(9)		
N(1)−H(1)···O(12)	149.89	N(2)−H(2)···O(13)	147.98
N(3)−H(3)···O(22)	100.72	N(4)−H(4)···O(23)	160.23
Torsion Angles			
C(17)−N(1)−C(12)−C(11)	142.3(3)	C(18)−N(2)−C(16)−C(11)	−145.1(3)

Table 5. Selected IR Bands and CRAMPS NH Chemical Shifts for Various Phosphate Ligands and Ca(II) Complexes[a]

	IR bands (cm^{-1})[a]			CRAMPS (ppm)
	ν(OH)	ν(NH)	ν(C=O)	δ NH
1	3430 (br)	3431	1690, 1673	9.5 (br)
2b	3430 (br)	3419	1678, 1667	14.1
3	3417 (br)	3226 (br)	1646	−
4	3418 (br)	3221 (br)	1671	−
5	3411 (br)	3335 (br), 3253 (br)	1678, 1650	13.2

[a] In the solid state (KBr).

This type of NH···O hydrogen bond formation was found in a Ca(II) phosphate complex with a triphenylacylamino ligand.[31]

Formation of NH···O Hydrogen Bonds in the Solid State. The selected IR bands of the ν(OH), ν(NH), and ν(C=O) region for **1**, **2b**, **3**, **4**, and **5** in the solid state are listed in Table 5. The downshifted broad OH bands for **1** and **2b** are due to the formation of hydrogen bonds with C=O or P−O oxygen in the solid state. The OH bands for **3**, **4**, and **5** originate from the water and methanol molecules coordinating to Ca(II) or Na(I) ions. The amide NH bands of **1** and **2b** appear around 3400 cm^{-1} as free NHs,[55] although the NH bands for **3** and **4** shift to 3226 and 3221 cm^{-1}, respectively. The large shifts of approximate 200 cm^{-1} from the free NH bands suggest the presence of strong NH···O hydrogen bonds formed in the phosphate dianion state. Actually, the distance between the two amide N and phosphate O atoms for **3** and **4** are within the possible range for hydrogen bonding. The amide ν(C=O) stretching band of **3** observed at 1646 cm^{-1} shifts about 24 cm^{-1} from that of **4**. Intermolecular OH···O=C hydrogen bonds between the amide C=O and water molecules exist in the crystal structure for **3**; however, the amide C=O for **4** is free from hydrogen bonding. The ν(NH) stretching bands for **5** are observed at 3253 and 3335 cm^{-1}, which are assignable to the

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amide NHs and ammonium NH, respectively.[31] The low-wavenumber shifted bands for **5** are also indicative of the formation of strong NH···O hydrogen bonds in the dianion state. The amide C=O stretching bands are observed at 1678 cm^{-1}, and the shifted bands at ˜1650 cm^{-1} are thought to originate from C=O4, which is coordinated to the Na ion.

CRAMPS is often used to detect each proton under different circumstances in the solid state.[56,57] The CRAMPS amide NH chemical shifts for **1**, **2b**, and **5** are 9.5, 14.1, and 13.2, respectively. The downfield shift of the amide NH chemical shifts also indicates the presence of hydrogen bonds with the amide groups.

Formation of NH···O Hydrogen Bonds in the Solution State. The formation of NH···O hydrogen bonds from the amide NHs to the phosphate in solution was determined by ^{1}H NMR spectroscopy. The amide NH chemical shifts for **5**, **2b** and **1** are observed at 11.56, 10.87, and 10.32 ppm, respectively. The NH signal in the phosphate monoanion, **2b**, appears downshifted by 0.55 ppm from that in the phosphoric acid state, and the NH signal in the phosphate dianion complex, **5**, was further shifted (+1.24 ppm). Thus, the NH···O hydrogen bonds to the phosphate oxygen atoms are not likely formed in the phosphoric acid state and are formed in the phosphate monoanion state. The stronger hydrogen bonds exist in the phosphate dianion state. The ^{1}H NMR results are consistent with the IR.

Construction of Novel Metal−Phosphate Structures with Bulky Amide Ligands. We first constructed the zigzag, cyclic-octanuclear Ca(II)- and hexanuclear Na(I) phosphate structure with an unusual metal coordination geometry using bulky amide ligands. All of the reported $Ca(O_3POR)$ or $Ca(O_3PR)$ complexes have polymeric structures, a one-dimensional chain, or a layer architecture.[32,33,36−39] Reported Na phosphate complexes are also polymeric.[40−42] These structures are schematically represented in Figure 5. The uncoordinated oxygen atom of the P=O bond tends to form a metal−oxygen bond which produces polymeric structures. In the complexes shown here, the oxygen atoms of the phosphate ligands chelate to the metal ions, which exist between the ligand alleys shown as white boxes (see Figure 5a). We call this kind of metal alley *symmetric*. The zigzag Ca(II) complex, **3**, has an alternative alley of the phosphate ligands and a hydrated site shown as black boxes (see Figure 5b). The cyclic-octanuclear Ca(II) complexes, **4**, provide a hydrated site inside the Ca(II) ions, and phosphate ligands are found outside (Figure 5c). The hexanuclear Na(I) complex, **5**, has the ligands between the trinuclear core, and its outside coordination site is occupied with methanol molecules (Figure 5d). The bulky benzoylamino ligands occupy the *unsymmetric* positions of phosphate ligands. Such an *unsymmetric* metal−phosphate ligand unit has been known to be present in the mononuclear Ca(II) with very bulky triphenylacetylamino groups, **4** (Figure 5e).[31] Our bulky amide ligands enable the production of an *unsymmetric* coordination environment because of steric congestion.

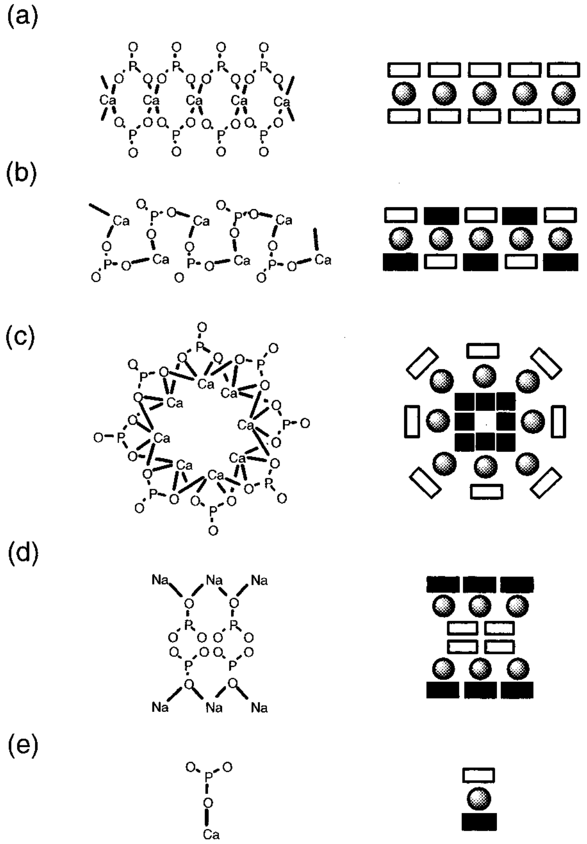

Figure 5. Schematic representation of (a) the one-dimensional structure of the reported Ca(II) complexes, (b) the zigzag-chain structure found in **3**, (c) the cyclic-octanuclear structure for **4**, (d) the hexanuclear structure for **5**, and (e) the mononuclear Ca(II) core[31] with *unsymmetric* ligand coordination. White and black boxes are the organic phosphate and other ligands, i.e., water molecules and/or methanol.

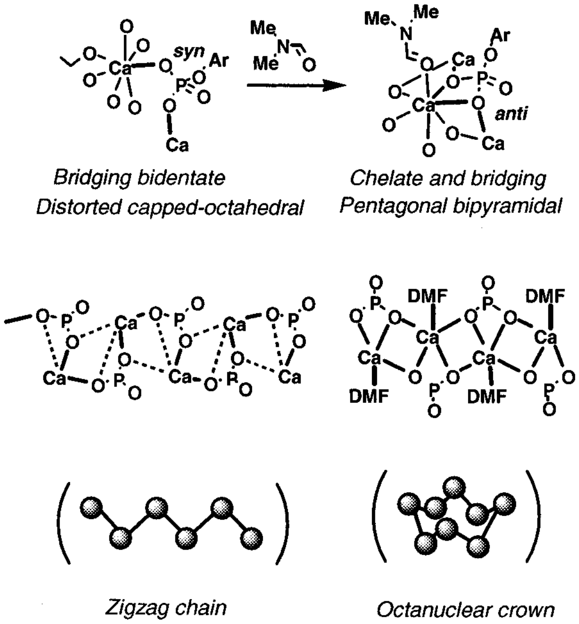

Figure 6. Schematic diagram of a structural difference between $[Ca^{II}\{O_3POC_6H_3(NHCOPh)_2(H_2O)_4(EtOH)\}_n$ (**3**) and $[Ca^{II}_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$ (**4**).

The infinite zigzag-chain structure of **3** transforms into the cyclic-octanuclear complex as shown in Figure 6. The reported transformation of the zinc phosphate structure occurs from a linear chain into a layer architecture via a ladder structure cooperated with decreasing numbers of the phosphate anion.[12,21] The transformation in our Ca(II) complex from a zigzag to a cyclic structure occurs by the coordination of the amide C=O

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of DMF without changing the metal/phosphate ratio. The zigzag-chains are stacked with each other due to the intermolecular OH···O=C hydrogen bonds involving the amide groups. The DMF molecule seems to be effective in removing the interactions to the amide C=O. Our bulky amide ligands are able to convert the formation of the intermolecular and intramolecular hydrogen bonds. The transformation from the zigzag structure to the cyclic-octanuclear structure is correlated with the formation of the intermolecular hydrogen-bond networks.

Conclusions

Novel zigzag-chain, cyclic-octanuclear Ca(II)- and hexanuclear Na(I) phosphate complexes were synthesized using bulky amide aryl dihydrogen phosphate ligands. The metal complexes with bulky amides have a unique *unsymmetric* ligand position. The zigzag structure transformed into a cyclic-octanuclear structure due to the change of coordination of DMF and the intermolecular hydrogen-bond network. The ligand design with amide groups is an intriguing approach for the regulation of intramolecular and intermolecular hydrogen bonds. In conclusion, synthesis of Ca(II) complexes using strategically designed bulky amide ligands will become very important for understanding biomineral Ca(II) structures found in biological systems and also for expanding new Ca(II) cluster chemistry.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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