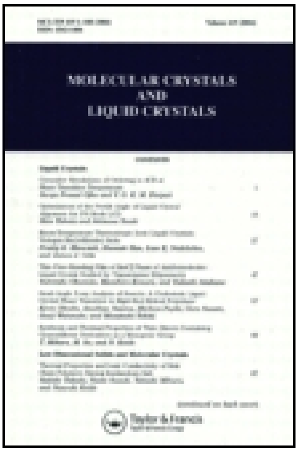

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# Zigzag-Chain, Cyclic-Octanuclear Calcium- and Hexanuclear Sodium Phosphate Complexes with Bulky Amide Ligands Involving a Network of Inter- and Intramolecular Hydrogen Bonds

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# Zigzag-Chain, Cyclic-Octanuclear Calcium- and Hexanuclear Sodium Phosphate Complexes with Bulky Amide Ligands Involving a Network of Inter- and Intramolecular Hydrogen Bonds

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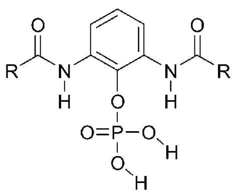
Novel zigzag-chain, cyclic-octanuclear Ca- and hexanuclear Na-phosphate complexes were synthesized using bulky amide aryl dihydrogen phosphate ligands. The metal complexes with bulky amides have a unique *unsymmetric* ligand position. The zigzag-chain structure transformed into a cyclic-octanuclear one in cooperating with the coordination of DMF molecule and reorganization of the intermolecular/intramolecular hydrogen bond networks.

Keywords: biomineral; calcium phosphate complex; NH···O hydrogen bonds; polynuclear complex; structural transformation

## INTRODUCTION

The polynuclear phosphate complexes with various metal ions and/or hydrogen bond donor ligands provide fascinating insight for the design of solid-state materials. Ca phosphate complexes are of special interest for their relevance to biological issues, and their structure in particular may yield clues for understanding the biomineralIization of Ca phosphate materials, such as bone and teeth[1]. It has been reported that synthetic metal phosphate complexes with small ligands have open-framework structures[2], in which intermolecular hydrogen bond networks play an important role for developing a variety of metal phosphate complexes[3-5].

**SCHEME 1**



R = - $CPh_3$ (**1**)

R = - Ph (**2**)

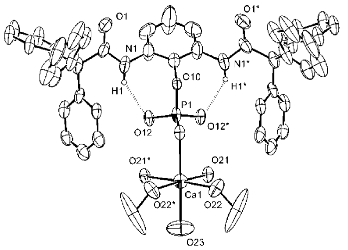


FIGURE 1 Molecular structure of $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOCPh_3)_2\}(H_2O)_3(MeOH)_2]$ (**3**)

Our previous research showed that the dissociation of metal-carboxylate bonds was prevented by the coordination between NH···O hydrogen bonds and carboxylate groups, because the NH···O hydrogen bonds lower the p$K_a$ value of the corresponding carboxylate[6,7]. Since phosphoric acid groups have two dissociative protons with different p$K_a$s, NH···O hydrogen bonds with them are thought to generate different distinctive properties as compared with a carboxylic acid groups. We designed a novel aryl phosphate ligand having intramolecular NH···O hydrogen bonds, as shown in Scheme 1. Ca complexes with phosphate ( $ROPO_3$ ) and phosphonate ligands ( $RPO_3$ ) are known to have polymeric structures, such as an one-dimensional structure and a layered structure. However, our designed amide ligands create bulkiness around the metal center which disrupt the formation of the polymeric coordination of Ca ions[8]. We present a report of crystal characterization of mononuclear, zigzag-chain, cyclic-octanuclear Ca and hexanuclear Na complexes having a bulky benzoylamino ligands by X-ray studies.

## CRYSTAL STRUCTURES

### Mononuclear Calcium Phosphate Complex

Figure 1 shows the molecular structure of a Ca complex, $[Ca\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOCPh_3)_2\}(H_2O)_3(MeOH)_2]$ (**3**)[8], having mononuclear core, which induced by the highly bulky phosphate ligand. The Ca center is in an octahedral geometry with the monodentate coordination of O12 of the phosphate ligand and with the oxygen atoms of three water molecules and two methanol, thus, the phosphate ligand coordinates in an *unsymmetric* fashion. The amide NH1 proton is intramolecularly hydrogen-bonded with uncoordinated oxygen O12. The first isolation of a mononuclear Ca phosphate complex is achieved by the extremely bulky amide ligand.

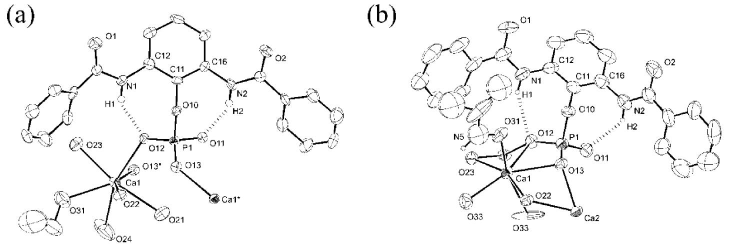


FIGURE 2 An unit structure of (a) $[Ca^{II}\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}(H_2O)_4(EtOH)]_n$ (**4**) and (b) $[Ca_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$ (**5**).

### Zigzag Chain

The molecular structure of Ca complex with less bulky phosphate ligand, $[Ca(O_3POC_6H_3(NHCOPh)_2(H_2O)_4(EtOH))_n$ (**4**)[9], is shown in Figure 2a. The Ca center is a seven coordinate structure in a capped-octahedral geometry. Four oxygen atoms of water molecules, O21, O22, O23, and O24, coordinate to Ca1 and O31 of the ethanol is in the capping position. The phosphate dianion ligands coordinate to Ca ions in a bridging bidentate mode and the unit forms an infinite zigzag chain structure. Each zigzag chain is covered by the bulky benzoylamino groups and gives a tubular ligand alley.

### Transformation to Cyclic-Octanuclear Calcium

A recrystallization of **4** in the presence of DMF gives an octanuclear Ca complex with DMF coordination, $Ca_8\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_8(O{=}CHNMe_2)_8(H_2O)_{12}]$ (**5**)[9], as shown in Figure 2b. Ca 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. An amide oxygen of DMF, O31, and a water molecule, O32, exist at each one of the axial positions. The two oxygen atoms (O12 and O13) of the coordinating ligand are in a tridentate-bridging mode to two Ca ions and each of the phosphate ligand binds to three Ca ions. The transformation of the coordination geometry of phosphate is induced by the coordination of DMF molecules.

The reconstruction of the hydrogen bonds networks is also observed during coordination of DMF. The zigzag chains for **4** are stacked with each other due to the intermolecular OH···O=C(amide) hydrogen bonds. The DMF molecule disrupts the intermolecular interaction to the amide groups and the zigzag-chain transformed into the cyclic-octanuclear Ca alley. The diameter of its ring is 8.513(2) Å, which forms the longest Ca···Ca (opposite) separation and eight water molecules coordinating to

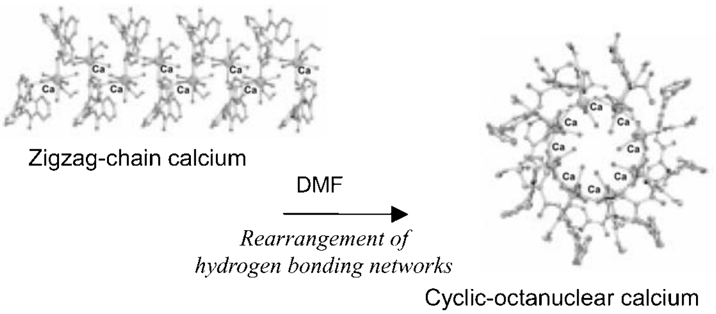


FIGURE 3 Transformation from zigzag-chian of **4** to cycylic-octanuclear structure of **5**

each of the Ca ions exist inside the Ca cluster ring. Our zigzag-chain Ca complex transforms into the cyclic-octanuclear structure cooperating with the reorganization of the intermolecular/intramolecular hydrogen bond networks (Figure 3).

## Hexanuclear Sodium Complex

Figure 4 shows the hexanuclear structure with a trinuclear core of $(NHEt_3)[Na_3\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_2(H_2O)(MeOH)_7]$ (**6**)[9]. A trinuclear core consists of two phosphate dianion ligands, three Na ions and one $NHEt_3^+$ cation. Both oxygen atoms in a phosphate dianion ligand and of methanol coordinate to the Na ions in $\mu_2$ 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. The coordination of the amide carbonyl oxygen, O4*, results in the dimerization of the trinuclear structure with *unsymmetric* coordination of

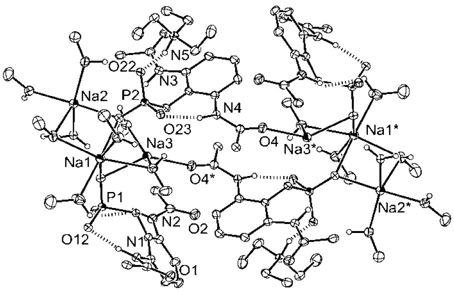


FIGURE 4 Molecular structure of $(NHEt_3)[Na_3\{O_3POC_6H_3\text{-}2,6\text{-}(NHCOPh)_2\}_2(H_2O)(MeOH)_7]$ (**6**)

the ligands.

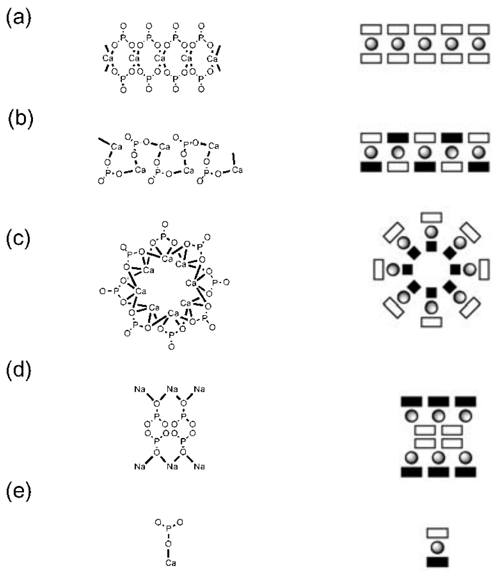


FIGURE 5 A schematic representation of (a) the one-dimensional structure of the reported Ca(II) complexes (b) the zigzag structure found in **4**, (c) the cyclic octanuclear structure for **5**, (d) the hexanucelar structure for **6** and (e) the mononuclear Ca(II) core[1] with *unsymmetric* ligand coordination. White and black boxes are the organic phosphate and other ligands, i.e. water molecules and/or metanol.

Novel Metal-Phosphate Structures with Bulky Amide Ligands.

All of the reported Ca($O_3$POR) or Ca($O_3$PR) complexes have polymeric structures, a one-dimensional chain and layer structure. Reported Na phosphate complexes are also polymeric. In the complexes shown here, the oxygen atoms of the phosphate ligands chelate to the metal ions, which exist between the *symmetric* ligand alleys shown as white boxes (Figure 5a). The zigzag Ca complex, **4**, has an alternative alley of the phosphate ligands and a hydrated site shown as black boxes (Figure 5b). Both cyclic octanuclear Ca complexes, **5**, and hexanuclear Na complex, **6**, also have *unsymmetric* positions of the ligands.(Figure 5c, 5d) Such an *unsymmetric* metal-phosphate unit has been know to be present in the mononuclear Ca with very bulky triphenylacetylamino groups, **4** (Figure 5e)[9]. Our bulky amide ligands enable to produce an *unsymmetric* coordination environment because of steric congestion.

## CONCLUSIONS

Novel zigzag chain, cyclic octanuclear Ca- and hexanuclear Na-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/or intermolecular hydrogen bonds. In our conclusion, synthesis of Ca complexes using strategically-designed bulky amide ligands will become very important for understanding biomineral Ca structures found in biological systems and also for expanding new Ca cluster chemistry.

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