Frameworks of amino acids: synthesis and characterization of two zinc phosphono-amino-carboxylates with extended structures

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Two α-amino acids, 3-phosphono-2-aminopropionic and 4-phosphono-2-aminobutyric, are used to link zinc atoms in three-dimensional structures where the three phosphonic and one of the carboxylic oxygen atoms coordinate to the metal, while the protonated amino groups and the second carboxylic oxygen atom are not coordinated and remain terminal in the voids of the framework.

Multifunctional ligands have attracted much interest in recent years mainly due to the possibility to build infinite frameworks by coordination to metal centers. Such hybrid inorganic–organic compounds have the potential for use in shape recognition, and more importantly, in stereoselectivity when chiral linkers are used. Linkers with two or more different functional groups are even more interesting since they can provide different modes of coordination, different stability, and different structural dimensionality and motifs. Extended structures of such organic moieties with two different end groups that are both coordinated to the metal centers are actually quite rare. Known and structurally characterized are one such amino-phosphonate with a zeolite-like structure, three carboxylate-phosphonates with layered structures, and three of the latter type but with three-dimensional framework structures. We have now taken one step further in the complexity, and have studied organic linkers with three different functional groups, i.e. species with an amino, carboxylic and phosphonic groups. Reported here are the structures and the IR and TGA characteristics of two framework compounds of zinc and phosphonated α-amino acids, Zn(O3PCH2CH(NH3)COO) (1) and Zn(O3PCH2CH(NH3)COO) (2), where the zinc atoms are coordinated by oxygen from the phosphonic and the carboxylic groups. Our ultimate goal is to achieve layered compounds with non-coordinated carboxylic and amino groups that are potential candidates for stereoselective intercalation due to the chiral α-carbon. In the pursuit of this same goal, layered inorganic compounds such as diphosphonates or carboxylates-phosphonates and poly-carboxylates, the organic species here are highly functionalized with hydrophilic groups, i.e. with the > C=O and NH3+ functionalities. These functional groups point toward the one-dimensional inter-linker apertures (4.36 A – O diameter) that exist along the b direction (Fig. 1), and are hydrogen bonded between themselves. The structure of compound 2 presents very similar features. Its carboxylic groups are also coordinated via only one oxygen atom, and therefore, the second one is terminal, and the amino groups are again protonated to –NH3+ (Fig. 2 and in the TOC). The other oxygen of the latter is noncoordinated as is the protonated amino group of the amino acid. Thus, unlike other examples of bi-coordinated organic moieties such as diphosphonates or carboxylates-phosphonates and poly-carboxylates, the organic species here are highly functionalized with hydrophilic groups, i.e. with the > C=O and NH3+ functionalities. These functional groups point toward the one-dimensional inter-linker apertures (4.36 A – O diameter) that exist along the b direction (Fig. 1), and are hydrogen bonded between themselves.

The structure of compound 1 is a hybrid of alternating inorganic and organic layers (Fig. 1). The inorganic layers, made of oxygen-connected tetrahedra centered by phosphorus and zinc, are linked by the amino acid molecules. The connectivity is achieved via the carbon–phosphorus bond of the phosphonated amino acid and with the coordination of one of the carboxylic oxygens to Zn (Fig. 1 and in the TOC). The other oxygen of the latter is noncoordinated as is the protonated amino group of the amino acid. Thus, unlike other examples of bi-coordinated organic moieties such as diphosphonates or carboxylates-phosphonates and poly-carboxylates, the organic species here are highly functionalized with hydrophilic groups, i.e. with the > C=O and NH3+ functionalities. These functional groups point toward the one-dimensional inter-linker apertures (4.36 A – O diameter) that exist along the b direction (Fig. 1), and are hydrogen bonded between themselves.
The vibrations of the phosphonic groups are observed in the slightly differently bonded carboxylic groups in the compound. For compound \( \text{Zn(O_3PCH_2CH_2CH(NH_3)COO)} \), the antisymmetric and at 1446 and 1429 cm\(^{-1}\) vibrations are observed for compound \( \text{Zn(O_3PCH_2CH_2CH(NH_3)COO)} \), respectively, while doublets at 1636 and 1621 cm\(^{-1}\). The splitting is due to the composite linkers. All pendant amino groups and carboxyl functionalities COOH and NH\(_3\), and the chiral \(-\text{carbon for a } \alpha\)-carbon for a variety of intercalation and chiral molecular recognition reactions.

Such supported amino acids can be used for a number of organic reactions in the interlayer spacing, including formation of peptide bonds and longer chains of different residues. The two compounds presented here are not layered or microporous, and guest molecules can not access the inside of the structures, but they clearly have the right structural motifs and are on the right track towards more open frameworks.

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Notes and references


