On a Possible Role of Dicarboxylate Ions in the Formation of Open-framework Metallophosphates

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Three dicarboxylic acids (oxalic, malonic and terephthalic) were investigated as possible pillars in the formation of metallophosphates with extended structures in the presence of 1,2-diaminopropane (DAP) as a structure-directing agent. Only the oxalate ion was proven to be a suitable building block in the formation of hybrid networks. The terephthalate ion seems to possess the ability to be structurally involved in lattice formation, although not in networks of the hybrid type. The malonate ion in this system showed no propensity towards lattice formation, i.e., malonic acid merely exits as an intercalated species inside the 2-D zincophosphate structure. Different pillar-functioning ability has been attributed to structural differences of the three dicarboxylate ions.

INTRODUCTION

An extremely active area in the materials chemistry is certainly the synthesis and structural characterization of novel open-framework solids. A real research eruption was initiated by the development of aluminophosphate molecular sieves.1,2 Their thermal stability and structural versatility has promised novel applications in the areas of catalysis, separation, ion exchange, electronics, optics and magnetics. Also, there have been considerable efforts of the preparation of open-frameworks based on transition metal phosphates because of their catalytic and magnetic properties.

Increased interest has been recently directed towards a rational design of new solid-state architectures. Careful selection of organic ligands as building blocks in the formation of novel inorganic-organic (hybrid) frameworks provides a promising route for advanced crystal engineering.3 Thus, various binding modes of the carboxylate group result in the formation of materials with unusual structures and properties.4,5 In these structures, the metal-organic frameworks are held together by metal-ligand interactions. The robustness of the networks depends on the strength and dimensionality of the bonds.

The existence of honeycomb architectures of transition metal oxalates indicates that oxalate ions could play an important building block role in the formation of open-framework solids. Indeed, an unusual aluminophosphate, which contains oxalate ions covalently bonded to the framework, has been reported.6 Also, an inorganic-organic hybrid possessing the structure similar to that

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of gmelinite is formed by linkage of the AlO₂, PO₄ and oxalate units. A large circular 12-member channel is a major structural feature of the hybrid framework.

This paper describes briefly our results in the synthesis of inorganic-organic solids with open architectures. We have investigated the oxalate, malonate and para-benzene dicarboxylate (terephthalate) ions as potential building blocks in the formation of hybrid networks.

EXPERIMENTAL

All syntheses were carried out hydrothermally using 1,2-diaminopropane (DAP) as a structure-directing agent. Reaction mixtures with the molar ratio of reactants of 1:6:1:2:100 (aluminum isopropoxide, zinc acetate or ferric chloride, orthophosphoric acid, dicarboxylic acid (or terephthalic acid, disodium salt), DAP and water, respectively) were thoroughly homogenized with an Ultra-Turrax mixer and left to crystallize at 130–160 °C for 4–6 days.

The lattice energy calculations were carried out using the GULP program. Spinning sideband analysis in 13C MAS NMR spectra was performed with the “dmfit” program.

RESULTS AND DISCUSSION

Crystallization of the reaction mixture in which aluminum isopropoxide was used as the metal component and oxalic acid as dicarboxylic acid gave a new 3-D aluminooxalato phosphate (APOX), consisting of aluminophosphate layers pillared by oxalate ions. The layers contain two distinct crystallographic sites for aluminum: one tetrahedral and one octahedral with the same population. The layers are composed of AlO₆, AlO₄ and PO₄ polyhedra giving double chains, which are interconnected through Al-O-P-O-Al bridges. Oxalate ions are quadridentately bonded by participating in the coordination of AlO₆ and by bridging the layers. A hybrid 12-member ring channel is formed that runs through the structure and hosts diprotonated DAP and water molecules (Figure 1).

It is worth noticing that the crystallization of a reaction mixture in which oxalic acid was not used, but in which the molar ratio of all other reactants was similar to that used in the APOX synthesis, and which crystallized under similar conditions (temperature, duration of crystallization), gave a chain-like aluminophosphate (Figure 2). During this crystallization, DAP partially decomposed yielding NH₄⁺ so that in this system both the doubly protonated DAP and NH₄⁺ ions exerted a structure-directing role. This raises the question of the role of oxalate ions when present in the reaction mixture. Recently, Rao and co-workers have found that amine oxalate intermediates may play a role in the formation of metal oxalates with extended architectures. They have obtained zinc oxalates of different dimensionalities (1-D, 2-D and 3-D) by reaction of various amine oxalates with zinc ions. Taking this into account, it seems likely that in the APOX synthesis the (Al₂O₆)- and (P₂O₇)-polyhedra start to cross-link with oxalate ions around the DAP species at an early stage of crystallization. In this manner DAP is trapped and stabilized within the framework and undergoes no partial decomposition observed in the absence of oxalate ions.

The reaction mixture analogous to that used in the APOX synthesis, but containing Fe³⁺ ions instead of Al³⁺, yielded the open-framework iron(III) phosphate-oxalate (FPOX). The iron(III) phosphate layers are bridged by oxalate units bonded to octahedrally coordinated iron centers, resulting in the formation of large one-dimensional 12-member channels. The channels run perpendicular to the iron phosphate layers and contain DAP and water molecules. The doubly protonated DAP is positioned in an asymmetric manner, thus creating different environments for the Fe atoms situated across one another on the sides of the channel (Figure 3). This indicates that the amine component can also affect the magnetic properties of metallophosphates (Figure 4).
However, it is interesting that in the absence of oxalate ions the crystallization does not yield any porous phosphate phase; instead, phosphosiderite (FePO₄·2H₂O) is formed from the reaction mixture as a single phase. Hence, it again appears that cross-linking of the (Fe, O)- and (P, O)-polyhedra with oxalate ions around the DAP species is crucial in the FPOX formation.

It is not surprising that FPOX contains no tetrahedrally but only octahedrally coordinated Fe³⁺ ions. For example, the lattice energy calculations reveal that the hypothetical isomorphous substitution of Al³⁺ by Fe³⁺ in APOX would give different energy effects, depending on the particular Al³⁺-site that undergoes substitution. Specifically, a partial substitution in APOX that would result in the Fe³⁺ ions being located only at octahedral Al-sites is by about 60 kJ per mole Al more favorable than the substitution occurring only at tetrahedral Al-sites. Thus, the presence of only octahedral Fe-sites in FPOX reflects a general preference of Fe³⁺ for octahedral vs tetrahedral coordination geometry.

Use of malonic instead of oxalic acid gives a crystalline product (ZPMAL) only in the case when zinc ions are involved in the reaction mixture. However, malonic acid in ZPMAL is only an intercalated species along with DAP and ammonium cations (all of them being disordered over the same sites, which are only partially occupied). The zinc phosphate product has a 2-D crystal structure (Figure 5) built up of parallel inorganic layers, which are held together through hydrogen bonding with the intercalated species. The latter are also mutually interconnected by hydrogen bonds. An eight-member ring channel runs through the macroanionic zinc phosphate sheet. During the crystallization of ZPMAL, the DAP species partially decomposed yielding NH₄⁺. This behavior is similar to
that observed in the chain-like aluminophosphate. This can serve as an additional support to the suggestion that dicarboxylate ions, in cases when they participate in the formation of networks, get involved in the reaction in an early stage of crystallization. Namely, since the malonate ion does not exhibit a cross-linking property in the ZPMAL synthesis, the DAP species is not trapped and stabilized within the framework at the start of crystallization and its partial decomposition occurs.

Terephthalate ions act as multidentate bridging ligands and have been used in many synthetic systems because they form short bridges via one carboxylato group or long bridges via the benzene ring. Accordingly, the terephthalate ions have been promising building units for designing polymeric magnetic systems. In the present study, we used two sources of terephthalate ions: disodium salt of terephthalic acid, and a reagent obtained by dissolution of terephthalic acid in a DAP solution. The latter system gave no crystalline products. The use of terephthalate ions from the disodium salt reagent did not promote crystallization of metallophosphates. Still, a crystalline product does form, but only from a reaction system containing the zinc ions, the terephthalate ions and DAP in the molar ratio of 4:2:3, respectively. The product (Zn/DAP/TA) is thermally stable up to 400 °C. In the range of 400–450 °C, there is a mass loss corresponding to the DAP content. Solid-state $^1$H–$^{13}$C CPMAS NMR measurements of terephthalic acid, the as-prepared Zn/DAP/TA, and the thermally treated Zn/DAP/TA (at 420 °C, in an oxygen atmosphere) show resonance contribution of the carbon belonging to carboxylic groups with the center band at about 174–176 ppm and two different contributions of the carbon from the aromatic ring in the range of 131 to 138 ppm (Figure 6). Resonance lines in the spectrum of the thermally treated Zn/DAP/TA are broader than in the as-synthesized material, suggesting that there is a large local disorder in the former. This could be caused by a partial loss of crystallinity of Zn/DAP/TA, though it could indicate that the terephthalate species in the Zn/DAP/TA product are structurally involved in the lattice formation. Figure 7 and Table I show that the chemical shift anisotropy (CSA) does change substantially for the carbon nuclei in carboxylic groups in the as-prepared and in the thermally treated

![Figure 4. Room temperature Mössbauer spectrum showing the presence of Fe$^{2+}$ in two different local environments.](image)

![Figure 5. 2-D ZPMAL structure, (NH$_4$)$_4$[Zn$_3$P$_3$O$_8$H$_2$](COOH(CH$_2$)COOH)$_{0.25}$[Zn$_{0.75}$P$_3$O$_{11}$OH$_2$–], (ZnO$_4$ tetrahedra are dark, PO$_4$ tetrahedra are white; organic molecule atoms are open circles).](image)
samples compared to terephthalic acid itself. This also suggests that in the Zn/DAP/TA material the terephthalate groups create a network of bridges via (Zn, O)-polyhedra (such as in Refs. 18–21), i.e., the terephthalate ion is not present just as a simple anion as it is, for example, in tetra-aqua(2,2'-bipyridine)zinc(II) terephthalate.22 The oxygen NMR measurements could certainly give a more precise answer; however, the oxygen NMR is very demanding due to the low natural abundance of the NMR-active $^{17}$O isotope and due to its high quantum number (5/2) that induces substantial quadrupolar line-broadening. More results are expected from the Rietveld powder diffraction analysis, which is currently in progress.

CONCLUSIONS

Only the oxalate ion has proved to be a suitable building block in the formation of hybrid networks. Although it has been found that the malonate ion has the ability to be structurally involved in a 3-D lattice formation,23 in the present system this ion has not shown any propensity towards hybrid lattice formation; instead, malonic acid stays intacta in the lattice interstices. Also, in this system, the terephthalate ion shows only the ability to be structurally involved in lattice formation, but not in networks of the hybrid type.

This difference in behavior of the malonate ion vs. oxalate ions could be related to their structural differences. Namely, the strict resonance-induced planarity of the free oxalate ion makes these anions rather rigid structural units of fixed geometries, which can therefore readily function as building blocks of hybrid network systems. In contrast, the complete rotational freedom around two C-C axes in the malonate ion renders this anion a very flexible species, which can be present in reaction systems in a variety of conformations. It is this absence of structural rigidity that could prevent the malonate ion from being a suitable building block of hybrid network structures.
The reason why the terephthalate ion does not participate in hybrid lattice formation can be attributed to the lack of a significant chelate effect when this ion coordinates to a metal center. The terephthalate ion can in general coordinate in the chelate manner but the four-member ring (I) that thereby necessarily forms is far less stable than the five-member chelate ring (II) arising in the case of the oxalate ion.

### REFERENCES


### TABLE I.

Results of spinning sideband analyses of carbon MAS spectra of terephthalic acid and of the as-prepared Zn/DAP/TA sample. In both spectra, a contribution from carboxylic carbon nuclei and two contributions from aromatic carbon nuclei could be resolved. In the latter sample, contribution of carbon nuclei from the template molecules was analyzed as well. For each contribution, the isotropic chemical shift ($\delta_{\text{iso}}$), chemical shift anisotropy ($\delta_{\text{CSA}}$), and the asymmetry parameter ($\eta$) were determined.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>$\delta_{\text{iso}}$ / ppm</th>
<th>$\delta_{\text{CSA}}$ / ppm</th>
<th>$\eta$</th>
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<tr>
<td>Terephthalic acid carboxylic C</td>
<td>173.7</td>
<td>-61</td>
<td>0.75</td>
</tr>
<tr>
<td>aromatic C–1</td>
<td>133.0</td>
<td>-118</td>
<td>0.7</td>
</tr>
<tr>
<td>aromatic C–2</td>
<td>129.7</td>
<td>-118</td>
<td>0.75</td>
</tr>
<tr>
<td>As-synthesized sample carboxylic C</td>
<td>175.7</td>
<td>-72</td>
<td>0.9</td>
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<tr>
<td>aromatic C–1</td>
<td>137.1</td>
<td>-117</td>
<td>0.7</td>
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<tr>
<td>aromatic C–2</td>
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<td>-122</td>
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<tr>
<td>template C</td>
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SAŽETAK

Uloga dikarboksilat iona u nastajanju metalofosfata s poroznim strukturama

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Ispitana je mogućnost ugradnje tri carboksilne kiseline (oksalne, malonske i tereftalne) u strukturu poroznih metalofosfata, uz 1,2-diaminopropan kao strukturnog usmjeritelja. Jedino oksalatni ion može biti građevna jedinica pri nastajanju hibridne strukture. Tereftalat ion ima sposobnost uključivanja u nastajanje kristalne rešetke, ali ne hibridnoga tipa. Malonat ion u ovom sustavu ne pokazuje sposobnost ugradnje u kristalnu rešetku već ostaje okludiran unutar 2-D cinkofosfatne strukture. Do navedenih različitosti dolazi uslijed razlika u strukturi oksalne, malonske i tereftalne kiseline.