4620 *Inorg. Chem.* **2010**, *49*, 4620–4625
DOI: 10.1021/ic100205n

Inorganic Chemistry
Article

# Synthesis and Spectroscopic and Computational Characterization of $Zn_4O$(Alicyclic or Aromatic Carboxylate)$_6$ Complexes as Potential MOF Precursors

**Sándor B. Ötvös,[†] Ottó Berkesi,*[,†] Tamás Körtvélyesi,[†] and István Pálinkó*[,‡]**

[†] *Department of Physical Chemistry and Material Science, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720 Hungary, and* [‡] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

Received February 2, 2010

Potential metal−organic-framework precursors, $Zn_4O$ complexes with various alicyclic or aromatic carboxylate ligands, were prepared, in many cases quantitatively, from ZnO and the relevant carboxylic acids in the presence of trace amounts of water. The complexes obtained were characterized with various classical (titration) and instrumental (IR and NMR spectroscopies) methods and molecular modeling (PM3 and PM6 semiempirical quantum chemical methods and HF/6-31G** ab initio calculations). Structural peculiarities reflected in the success or failure in the synthesis could be rationalized with the combination of IR and NMR spectroscopies and molecular modeling.

## Introduction

People have already prepared, used, and studied to some extent soaps in ancient times. Scientific interest gradually emerged: long-chained fatty acid sodium salts became every day tools of chemists, especially of colloid chemists, and related surface-active materials became interesting for molecular biologists. Other, more esoteric metal ion carboxylic acid systems have also been investigated, and the obtained results and correct or occasionally false interpretations found their way into textbooks, helping or hindering further research. Exactly this happened to zinc carboxylate soaps. For a long time, these systems were not in the forefront research; nevertheless, some researchers were active in this area, and it was found that with acetic acid, under certain conditions, a $Zn_4O(CH_3COO)_6$ complex could be formed.[1] Its crystal structure was also determined some time later.[2] Tetrahedral arrangement was found around a central O atom, and carboxylate bridges connected the Zn atoms to each other in a way that the geometric arrangement around each Zn atom was also tetrahedral. It was generally accepted that the synthesis conditions were demanding; water, even in traces, was thought to be harmful. The extreme water sensitivity of this complex entered authorative textbooks[3,4] too, hindering somewhat the research activity in this area. Later research pointed out that water was a crucial player in this system indeed. However, its presence caused no harm; moreover, it was a prerequisite of complex formation.[5−7] The accumulated experimental results allowed us to propose a novel mechanism for the formation of the complex having three steps: (i) in the first step occurring in the solid-state, $Zn(RCOO)_2$, a planar polymeric structure is formed, (ii) the polymeric structure remains but transforms to a chain during dissolution, and, finally, (iii) the polymeric structure is in equilibrium with $Zn_4O(RCOO)_6$. Water shifts the equilibrium toward complex formation, and the lack of interaction between the carboxylate chains also favors the formation of the complex.[8,9] In order to allow these factors to be operational, the presence of water, the appropriate solvent, high enough temperature, and carboxylic acids with chain sterically hindering interactions are necessary.[8,9] These findings made almost no echo in the scientific community and, generally, research activity has declined in this area. The topic was very much out of fashion until the first decade of this century, when a couple of papers appeared reporting the synthesis and some applications of a new class of materials called metal−organic-framework (MOF) substances (for some conceptual reviews, see refs 10 and 11, and issue 5 of

---

*To whom correspondence should be addressed. E-mail: palinko@chem.u-szeged.hu (I.P.), oberkesi@chem.u-szeged.hu (O.B.).

(1) Auger, V.; Robin, M. V. *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences* **1924**, *178*, 1546.

(2) Wyart, J. *Bull. Soc. Fr. Mineral.* **1926**, *49*, 148.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 607.

(4) Greenwood, N. N.; Earnshaw, A. *Chemistry of Elements*; Pergamon Press: New York, 1993; p 1411.

(5) Berkesi, O.; Dreveni, I.; Andor, J. A.; Goggin, P. L. *Inorg. Chim. Acta* **1991**, *181*, 285.

(6) Berkesi, O.; Dreveni, I.; Andor, J. A.; Mink, J. *Inorg. Chim. Acta* **1992**, *195*, 169.

(7) Berkesi, O.; Andor, J. A.; Jayasooriya, U. A.; Cannon, R. D. *Spectrochim. Acta* **1992**, *48A*, 147.

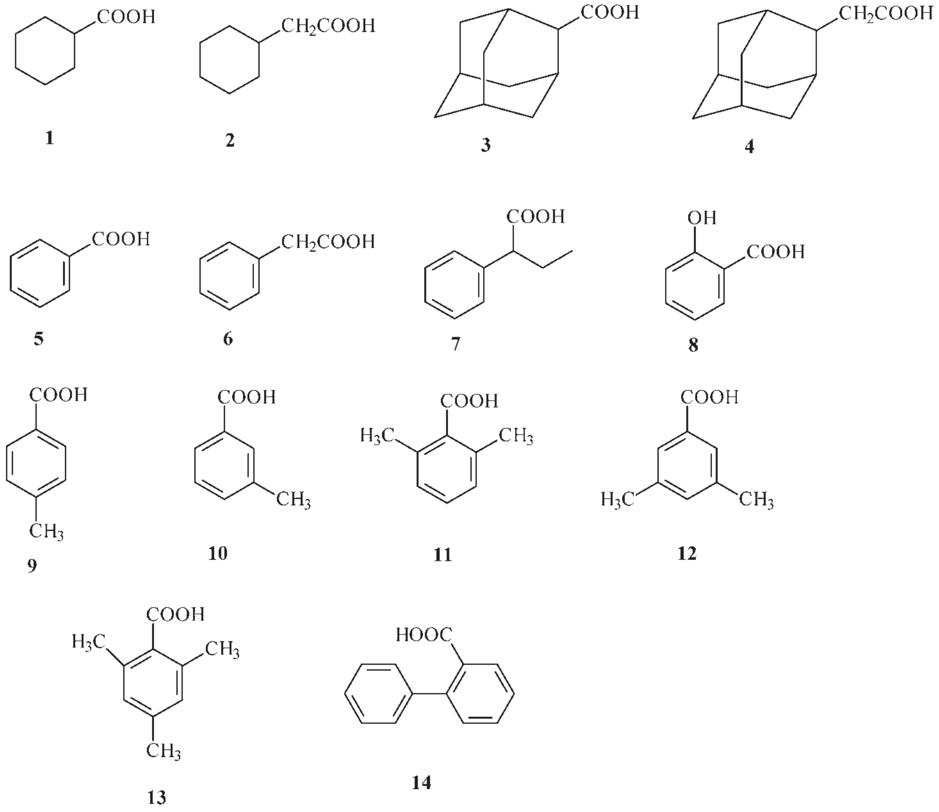
(8) Dreveni, I.; Berkesi, O.; Andor, J. A.; Mink, J. *Inorg. Chim. Acta* **1996**, *249*, 17.

(9) Berkesi, O.; Katona, T.; Dreveni, I.; Andor, J. A.; Mink, J. *Vib. Spectrosc.* **1995**, *8*, 167.

(10) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.

(11) Ockwig, N. W.; Friedrichs, O. D.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.

**Scheme 1**



*Chem. Soc. Rev.* in 2009[12] was entirely devoted to this topic). In some of the early MOF substances, the secondary building units (SBUs) were zinc carboxylate complexes of various kinds,[13−16] and the resulting MOF structures were either one-, two-, or three-dimensional[14] depending on the solvent and the base used. The SBU for the synthesis of MOF-5 was $Zn_4O$(1,4-benzenedicarboxylate).[16] This paper convinced us that it is worthwhile to pick up the study of $Zn_4O$-(carboxylate) complexes once again because many varieties have not been synthesized and characterized yet, some of the complexes may have peculiar properties worth investigating, and some may serve (perhaps after suitable modification) as useful synthons in the preparation of MOF materials with novel adsorption and/or catalytic properties.

## Experimental Section

**Materials and Methods of Synthesis.** During our work, the preparation of 14 $Zn_4O(carboxylate)_6$ complexes was attempted. The acid form of the ligands can be divided into two classes: alicyclic and aromatic carboxylic acids. The alicyclic carboxylic acids were as follows: cyclohexanecarboxylic acid (**1**), cyclohexylacetic acid (**2**), 1-adamantanecarboxylic acid (**3**), and 1-adamantylacetic acid (**4**). Benzoic acid (**5**), phenylacetic acid (**6**), 2-phenylbutanoic acid (**7**), *o*- (**8**), *p*- (**9**), and *m*-toluenecarboxylic acids (**10**), 2,6- (**11**) and 3,5-dimethylbenzoic acids (**12**), 2,4,6-trimethylbenzoic acid (**13**), and 2-biphenylcarboxylic acid (**14**) were the aromatic carboxylic acids (Scheme 1). All of them were high-purity commercial substances (purity was over 98%, and they were used without further purification), mostly from Sigma-Aldrich, but some of them were purchased from Merck, Reanal, BDH, and EGA Chemie. ZnO, $C_2Cl_4$, and *n*-decane solvents were also Sigma-Aldrich products.

Two methods were applied for synthesis of the complexes. *Method A*: A 1:2 ratio mixture of carboxylic acid and ZnO (Sigma-Aldrich) was thoroughly mixed in an achate mortar, and the intimate mixture was transferred to a round-bottomed flask equipped with a reflux condenser. Solvent was added in the quantity that the concentration calculated on the expected amount of the $Zn_4O$ complex was 0.01 M. The solution was heated to boiling, and then a few drops of water were added. Reflux was continued for several hours, and the progress of the reaction was followed by IR spectroscopy on samples withdrawn from time to time. The reaction was considered to be over when the band typical for the free carboxylic acid disappeared. If it did not, more ZnO and water were added to push the equilibrium toward complex formation. *Method B*: The clean and dry acids were intimately mixed with NaOH, and then the mixture was dissolved in water. After the addition of $ZnSO_4$ ($ZnSO_4 \cdot 7H_2O$; Sigma-Aldrich) and heating of the mixture to boiling, a white solid precipitated [$Zn(RCOO)_2$]. After it was dissolved in an apolar solvent (if it was soluble) and a trace amount of water was added to it, $Zn_4O$(carboxylate) was formed.

**Zinc Analysis.** The zinc content of the samples was determined with complexometric titration. First, the solid samples were dissolved in a mixture of *aqua regia* and concentrated perchloric acid. After a suitable aqueous solution was prepared, titration was performed with ethylenediaminetetraacetic acid in the presence of Eriochrome black T. The carbon contents were planned to be measured on a Euroglas TOC 1200 analyzer. Unfortunately, measurements were not successful, probably because after dissolution the liquid got partially stuck to the

---

(12) *Chem. Soc. Rev.* **2009**, *38* issue (5).

(13) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096.

(14) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.

(15) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.

(16) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

**Table 1.** Results of Zinc Analyis and Molecular Mass Measurements

| | zinc content (m/m %) | | | molar mass (g/mol) | | |
|---|---|---|---|---|---|---|
| complex | calcd | measd | diff (%) | calcd | measd | diff (%) |
| $Zn_4O$(cyclohexanecarboxylate)$_6$ | 25.14 | 25.66 | 2.07 | 1040.50 | 1019.40 | −2.03 |
| $Zn_4O$(cyclohexylacetate)$_6$ | 23.26 | 23.73 | 2.05 | 1124.70 | 1102.10 | −2.01 |
| $Zn_4O$(benzoate)$_6$ | 26.04 | 25.68 | −1.40 | 1004.30 | 1018.60 | 1.42 |
| $Zn_4O$(2-phenylbutyrate)$_6$ | 20.81 | 20.87 | 0.30 | 1256.70 | 1253.00 | −0.29 |
| $Zn_4O$(*o*-methylbenzoate)$_6$ | 24.03 | 24.11 | 0.35 | 1088.50 | 1084.70 | −0.35 |
| $Zn_4O$(*p*-methylbenzoate)$_6$ | 24.03 | 23.30 | −3.05 | 1088.50 | 1122.80 | 3.15 |
| $Zn_4O$(*m*-methylbenzoate)$_6$ | 24.03 | 21.15 | −11.97 | 1088.50 | 1236.50 | 13.60 |
| $Zn_4O$(2,6-dimethylbenzoate)$_6$ | 22.31 | 22.07 | −1.07 | 1172.60 | 1185.30 | 1.08 |
| $Zn_4O$(3,5-dimethylbenzoate)$_6$ | 22.31 | 17.48 | −21.65 | 1172.60 | 1496.60 | 27.63 |
| $Zn_4O$(2,4,6-trimethylbenzoate)$_6$ | 24.81 | 20.73 | −0.39 | 1256.70 | 1261.60 | 0.39 |
| $Zn_4O$(2-phenylbenzoate)$_6$ | 17.91 | 17.55 | −1.98 | 1460.80 | 1490.30 | 2.02 |

wall of the flask; thus, the carbon content was seriously underestimated.

**Mass Measurement.** Molecular masses were measured with mass spectrometry using an AEI MS 902 instrument and perfluorotributylamine as a reference compound. The resolution was 10 000 (10% valley).

**IR Spectroscopy.** IR spectra were registered on a Bio-Rad Digilab Division FTS-65A/896 Fourier transform infrared (FT-IR) spectrophotometer equipped with a DTGS detector with a KBr window. The resolution was 4 $cm^{-1}$, and usually 128 scans were collected for a spectrum. A liquid cell of 0.1 mm thickness was used for measurements in solution. The 4000−400 $cm^{-1}$ region was used. Spectra were analyzed with the *WIN IR Pro 3.3* and *GRAMS/AI v.7* software packages.

**NMR Spectroscopy.** The $^1H$ and $^{13}C$ NMR spectra of $Zn_4O$(*p*-methylbenzoate)$_6$, $Zn_4O$(*o*-methylbenzoate)$_6$, and $Zn_4O$(2,6-dimethylbenzoate)$_6$ and those of the corresponding pure acids were measured on a Bruker DRX-500 FT-NMR in a $C_2Cl_4$/$CDCl_3$ solution at 303 K in NMR tubes of 5 mm diameter. The $^{13}C$ NMR spectra were registered with the JMOD pulse sequence.

**Computational Methods.** For modeling the structures of the complexes, the PM3[17] and PM6[18] semiempirical codes included in the *MOPAC 2009 v.8.318w*[19] and *PC GAMESS/Firefly 7.1 F*[20] packages and ab initio calculations with the 6-31G** basis set were used. Full geometry optimizations at the RHF level were performed, and the force matrices were also calculated. For the semiempirical calculations, PCs were used, while the computationally more expensive calculations were performed with an SGI Altix 3700 SSI cluster applied using the *GAMESS US*[21] package. In the semiempirical and the ab initio calculations, the gradient norms were $10^{-4}$ hartree/bohr and 0.05 kcal/Å, respectively.

The vibrational spectra were calculated from the force matrices and compared to the observed ones after appropriate scaling. Scaling factors were determined for the PM6 and HF/6-31G** calculations (for details, see the Supporting Information).

## Results and Discussion

**General Considerations Based on Zinc Analysis and Molecular Weight Measurements.** As the first step, let us survey the results of zinc analysis and mass measurement listed in Table 1.

It is clear that in most cases the difference between the expected and observed zinc contents is within experimental error. There were only two cases (ligands *m*-methylbenzoate and 3,5-dimethylbenzoate) when the obtained solid materials differed significantly from our expectations. This means that either the materials did not contain the $Zn_4O$ moiety or some other Zn-containing complexes were also formed.

To be able to learn what happened during the synthesis, additional tools were needed. IR spectroscopy proved to be suitable in following the complex formation and learning about the structures obtained.

**Complex Formation Studied by IR Spectroscopy.** Several methods were quoted in the experimental section of the articles describing $Zn_4O$ SBUs[13−16] as a tool to identify the structure, including FT-IR spectroscopy, but hardly any spectra were published and no characteristic bands of the structure were named and identified. Our previous studies proved, however, that the $Zn_4O$ complexes of aliphatic carboxylates showed a well-defined IR band pattern, and this pattern changed essentially if the structure was distorted or decomposed.[22] An aromatic ring bonded to the carboxylate group should significantly alter the couplings in the tetranuclear oxocarboxylato complex even more significantly because the $6\pi$ electrons of the aromatic ring and the $4\pi$ electrons of the carboxylate group are in conjugation. In addition, because of the very similar bond orders and reduced masses, the skeletal vibrations of the ring and the stretching vibrations of the carboxylate group can contribute to the normal vibrations more or less in the same proportion. The characteristic band of the $Zn_4O$ group, the antisymmetric stretching band of the group,[7] might also be influenced through the reduced masses by the atoms fixed in the para position to the carboxylate group.[23]

The complex formation reaction could be followed by IR spectroscopy through monitoring of the disappearance of the $\nu_{C=O}$ band of the pristine carboxylic acid, the appearance of the symmetric and asymmetric valence vibrations of the carboxylate group, and the asymmetric valence vibrations of the $Zn_4O$ moiety. These parts of the IR spectra are shown in Figure 1 using the cyclohexanecarboxylic acid ligand as the example (similar spectra for the other ligands are collected as Supporting Information).

---

(17) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209 (see also p 221).

(18) Stewart, J. J. P. *J. Mol. Model.* **2007**, *13*, 1173.

(19) Stewart, J. J. P. *MOPAC2009*, version 8.318W; http://OpenMOPAC.net.

(20) Granovsky, A. A. *PC GAMESS/Firefly* version 7.1.F; http://classic.chem.msu.su/gran/gamess/index.html.

(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(22) Berkesi, O.; Berenji, P.; Dreveni, I.; Körtvélyesi, T.; Andor, J. A.; Mink, J.; Goggin, P. L. *Vib. Spectrosc.* **2007**, *43*, 227.

(23) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra*; Dover Publications Inc.: New York, 1991.

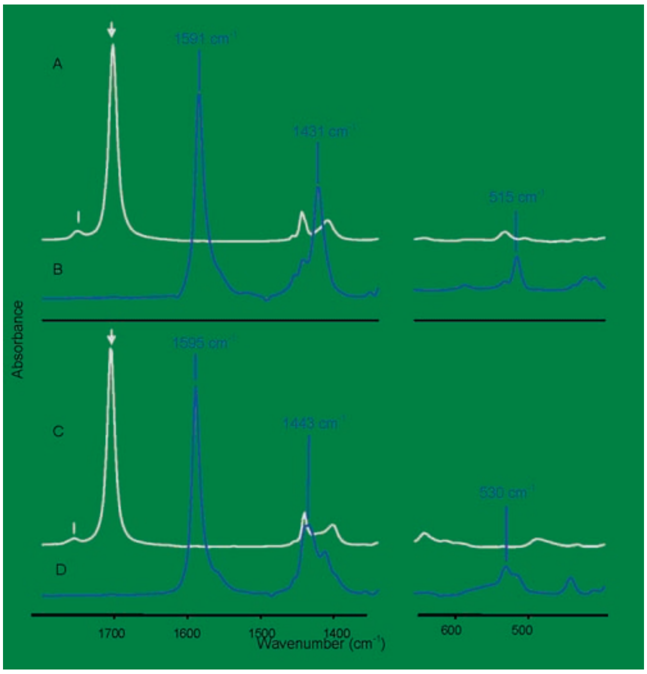


**Figure 1.** Vibrational spectra of (A) cyclohexanecarboxylic acid, (B) $Zn_4O$(cyclohexanecarboxylate)$_6$, (C) cyclohexylacetic acid, and (D) $Zn_4O$-(cyclohexylacetate)$_6$ dissolved in $C_2Cl_4$ in the 1800−1350 and 650−400 $cm^{-1}$ ranges. Band assignment: $\nu_{as,COO^-}$ 1591, 1595 $cm^{-1}$; $\nu_{s,COO^-}$ 1431, 1443 $cm^{-1}$; $\nu_{as,Zn_4O}$ 515, 530 $cm^{-1}$. $\nu_{C=O}$: carboxylic acid dimer, gray arrow; monomeric carboxylic acid, gray line.

The complex formation reactions went to completion for the cyclohexylacetic acid, 2-phenylbutyric acid, benzoic acid, *o*- and *p*-methylbenzoic acids, 2,6-dimethylbenzoic acid, and 2,4,6-trimethylbenzoic acid ligands giving solely the corresponding $Zn_4O$ complexes. These complexes were formed predominantly, but some unreacted acid remained, when 1-adamantanecarboxylic acid and 1-adamantylacetic acid were the ligands. As the IR spectra, registered when *m*-methylbenzoic acid or 3,5-dimethylbenzoate were the ligands, attested (see Figure 2 as an example for the *m*-methylbenzoic acid ligand; for the other ligands, see the Supporting Information), the reaction went to completion. The $\nu_{as,Zn_4O}$ band appeared; however, zinc dicarboxylate was also formed in appreciable amounts. This was not surprising; zinc analysis data have already indicated the nonuniformity of the material.

At the end of this section, we summarize the observed fundamental modes of the zinc carboxylate complexes using the already displayed spectra and those displayed in the Supporting Information section (Table 2).

It is to be noted that in complexes **1** and **3** $\nu_{a,Zn_4O}$ is lower than the others (that are largely uniform). In these structures, a rigid but nonaromatic structure is bonded to the central $Zn_4O$ tetrahedron; therefore, the reduced masses were increased.

Interestingly, the attempted syntheses with phenylacetic acid (**6**) were not successful with either method. After modeling of the ligands and complexes, sensible explanations for the success, partial success, and failure in the syntheses of the complexes could be given as follows.

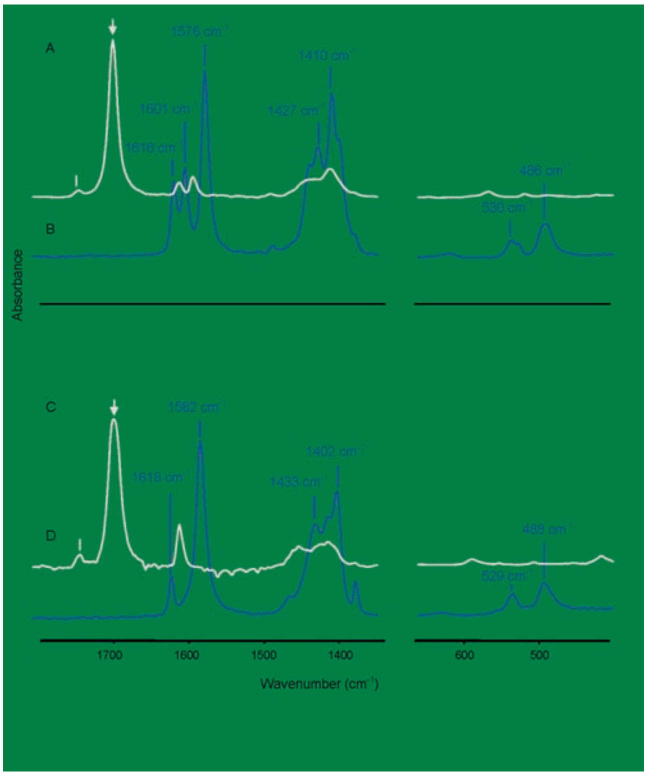


**Figure 2.** Vibrational spectra for (A) *m*-methylbenzoic acid, (B) a mixture of $Zn_4O$(*m*-methylbenzoate)$_6$ and Zn(*m*-methylbenzoate)$_2$, (C) 3,5-dimethylbenzoic acid, (D) a mixture of $Zn_4O$(3,5-dimethylbenzoate)$_6$ and Zn(3,5-dimethylbenzoate)$_2$ dissolved in $C_2Cl_4$ in the 1800−1350 and 650−400 $cm^{-1}$ ranges. Band assignment: $\nu_{as,COO^-}$ 1576, 1582 $cm^{-1}$, $\nu_{s,COO^-}$ 1410, 1427, 1402, 1433 $cm^{-1}$, $\nu_{as,Zn_4O}$ 530, 529 $cm^{-1}$. $\nu_{C=O}$: carboxylic acid dimer, gray arrow; monomeric carboxylic acid, gray line.

**Table 2.** Characteristic Fundamental Modes of Zinc Carboxylate Complexes ($cm^{-1}$)

| $Zn_4O$(carboxylate) complexes | $\nu_{a,COO}$ | $\nu_{s,COO}$ | $\nu_{a,Zn_4O}$ |
|---|---|---|---|
| **1** | 1591 | 1431 | 515 |
| **2** | 1595 | 1443 | 530 |
| **3** | 1591 | 1427 | 509 |
| **4** | 1595 | 1418 | 529 |
| **5** | 1608 | 1417 | 528 |
| **6** | polymerization occurred instead of complexation | | |
| **7** | 1601 | 1418 | 522 |
| **8** | 1611 | 1404 | 527 |
| **9** | 1576 | 1427 | 530 |
| **10** | 1605 | 1416 | 525 |
| **11** | 1594 | 1403 | 525 |
| **12** | 1582 | 1433 | 529 |
| **13** | 1590 | 1406 | 529 |
| **14** | 1601 | 1418 | 522 |

**Modeling of the Structures and the Measured IR Spectra.** Three examples will be shown here; for the other structures and simulated spectra, see the Supporting Information.

Figure 3 shows the equilibrium geometry of the $Zn_4O$-(cyclohexanecarboxylate)$_6$ complex preoptimized with the PM3 code and further optimized by the PM6 code.

The starting complex was constructed using the crystal structure of $Zn_4O$(formate)$_6$,[24] and then it was built further to arrive at the target complex. It is to be seen that the cyclohexyl groups are attached to the $Zn_4O$

---

(24) Hiltunen, L.; Leskela, M.; Makela, M.; Niinistö, L. *Acta Chem. Scand.* **1987**, *A41*, 548.

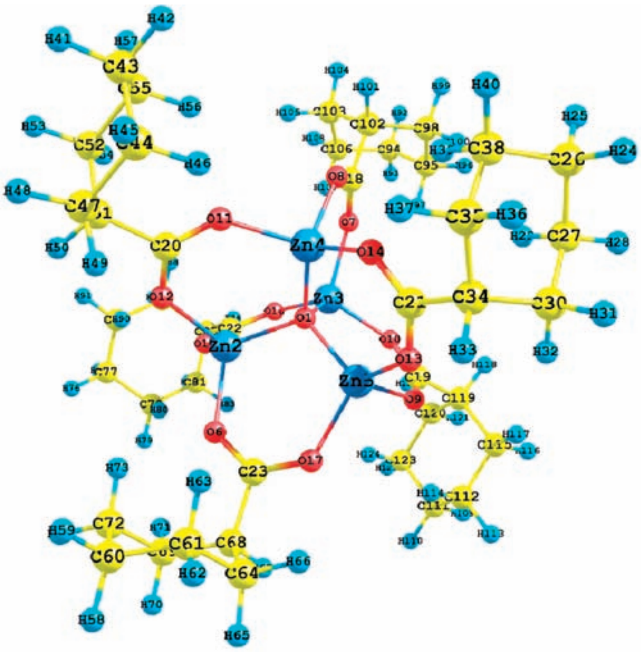


**Figure 3.** Stick-and-ball model of $Zn_4O$(cyclohexanecarboxylate)$_6$ optimized by the PM6 method.

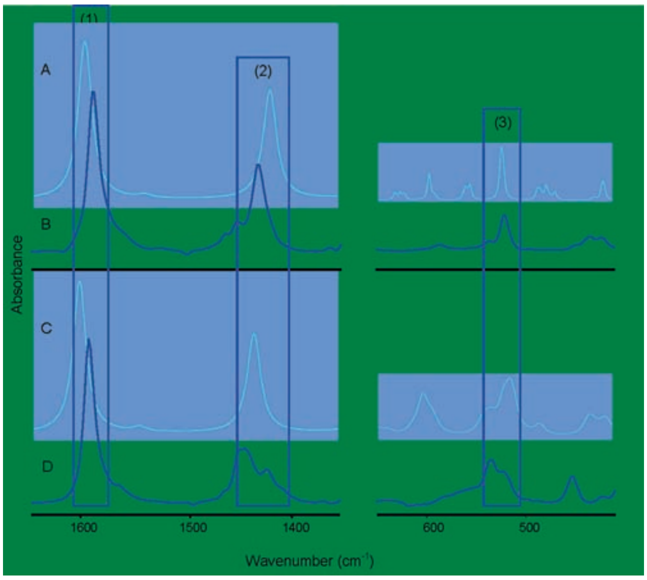


**Figure 4.** PM6 simulated and scaled (blue background) and observed (green background, dissolved in $C_2Cl_4$) spectra of $Zn_4O$(cyclohexanecarboxylate)$_6$ (traces A and B) and $Zn_4O$(cyclohexylacetate)$_6$ (traces C and D) in the 1650−1350 and 650−400 cm$^{-1}$ ranges. Band assignment: $\nu_{as,COO^-}$ (1); $\nu_{s,COO^-}$ (2); $\nu_{as,Zn_4O}$ (3).

nucleus axially, practically wrapping it. Similar arrangements were found with the other complexes as well.

The observed and simulated spectra in the 1650−1350 and 650−400 cm$^{-1}$ wavenumber regions, after appropriate scaling (for the scaling procedure, see the Supporting Information), are displayed in Figure 4 (the observed and simulated spectra of the $Zn_4O$(cyclohexylacetate)$_6$ complex are also included).

The simulated spectrum reproduces the observed one quite well. In the lower wavenumber region, coincidence is excellent. Besides the positions of the bands, even the intensity ratios could be reproduced well.

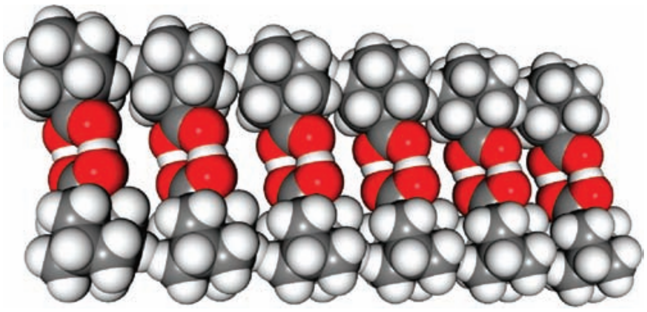


**Figure 5.** Model of the agglomerate of 1-adamantanecarboxylic acid calculated by the PM6 method (red, O; gray, C; white, H).

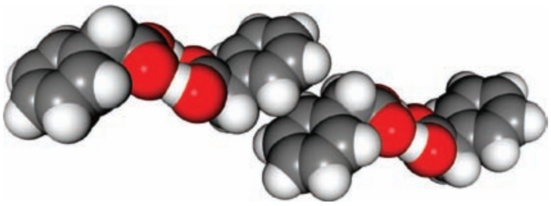


**Figure 6.** Dimer of the phenylacetic acid dimers kept together with CH$\cdots\pi$ interaction.

The 1-adamantanecarboxylic acid and 1-adamantylacetic acid ligands seemed to be excellent linkers in producing $Zn_4O$-MOF materials because they are large and rigid and can be functionalized well. Unfortunately, the $Zn_4O$ complex formation did not go to completion with these ligands, whatever variations in the synthesis conditions were done. In our view, the reason for this failure, or putting it in a positive way, partial success, is the tendency of these adamantyl derivatives to aggregate, as the PM6 simulation indicates (Figure 5). From our earlier experience, we know[8,9] that little or no interaction among the ligands is advantageous for successful and efficient complex formation.

The strong tendency of phenylacetic acid dimers to aggregate through C−H$\cdots\pi$ interactions (Figure 6) even completely hindered the formation of the $Zn_4O$(phenylacetate)$_6$ complex.

**Structural Information from NMR Spectroscopy.** Modeling of the complexes with aromatic ligands (benzoate and *o*- and *p*-methylbenzoate anions) showed that the carboxylate groups in the complex and the corresponding benzoic acid rings were in one plane (see the Supporting Information). This conjugated arrangement is the reason that the intensities of the $\nu_{s,COO^-}$ bands were higher than those of the $\nu_{as,COO^-}$ bands (with nonaromatic carbocycles, the intensity ratio was the opposite). However, when the benzoate ligands contained methyl groups next to the complexing carboxylate (2,6-dimethylbenzoic and 2,4,6-trimethylbenzoic acids), the intensity ratios were similar to those found with the nonaromatic carbocycles. This is a hint that conjugation ceased to exist, probably because of steric congestion around the complexing site. Optimized geometries computed at the HF/6-31G** level gave further evidence (see the Supporting Information). Additional experimental evidence was provided with $^1$H and $^{13}$C NMR spectroscopies (Figure 7).

The figure contains parts of the spectra showing the signals of the methyl groups for the acids (*o*- and

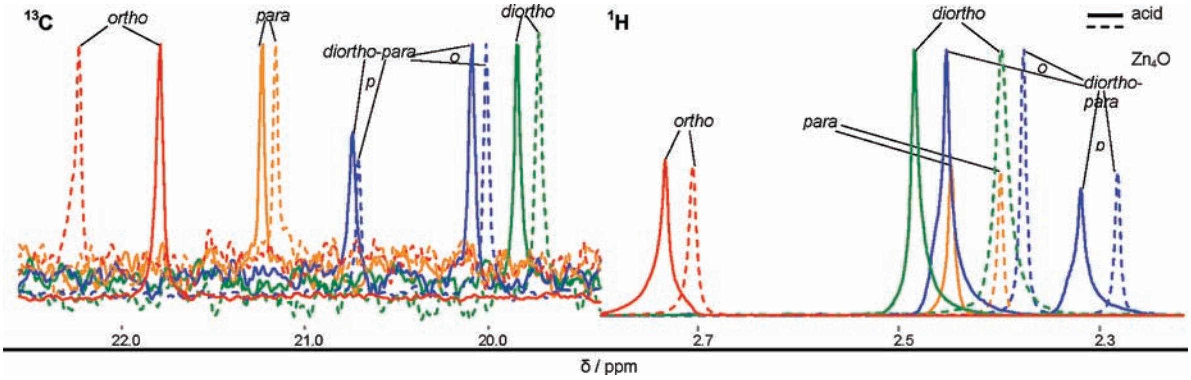


**Figure 7.** $^{13}$C and $^{1}$H NMR spectra: parts relevant to the methyl groups. Colors: red, *o*-methylbenzoic acid and the $Zn_4O$(*o*-methylbenzoate)$_6$ complex; orange, *p*-methylbenzoic acid and the $Zn_4O$(*p*-methylbenzoate)$_6$ complex; green, 2,6-dimethylbenzoic acid and $Zn_4O$(2,6-dimethylbenzoate)$_6$ complex; blue, 2,4,6-trimethylbenzoic acid and the $Zn_4O$(2,4,6-trimethylbenzoate)$_6$ complex.

**Table 3.** Chemical Shifts of the Methyl Groups for the Compounds Studied

| | $^{13}$C NMR | | | | $^{1}$H NMR | | | |
|---|---|---|---|---|---|---|---|---|
| | $\delta$ (ppm) | | $\Delta\delta$ (ppm) | | $\delta$ (ppm) | | $\Delta\delta$ (ppm) | |
| position of the methyl group | ortho | para | ortho | para | ortho | para | ortho | para |
| *o*-methylbenzoic acid | 21.7936 | | 0.4436 | | 2.7329 | | −0.0275 | |
| $Zn_4O$(*o*-methylbenzoate)$_6$ | 22.2372 | | | | 2.7054 | | | |
| *p*-methylbenzoic acid | | 21.2358 | | −0.0747 | | 2.4470 | | −0.0486 |
| $Zn_4O$(*p*-methylbenzoate)$_6$ | | 21.1611 | | | | 2.3984 | | |
| 2,6-dimethylbenzoic acid | 19.8403 | | −0.1181 | | 2.4846 | | −0.0871 | |
| $Zn_4O$(2,6-dimethylbenzoate)$_6$ | 19.7222 | | | | 2.3975 | | | |
| 2,4,6-trimethylbenzoic acid | 20.0883 | 20.7414 | −0.0788 | −0.0330 | 2.4525 | 2.3187 | −0.0770 | −0.0366 |
| $Zn_4O$(2,4,6-trimethylbenzoate)$_6$ | 20.0095 | 20.7084 | | | 2.3755 | 2.2821 | | |

*p*-methylbenzoic acids and 2,6-dimethyl- and 2,4,6-trimethylbenzoic acids) and the corresponding complexes.

There was some diamagnetic shift due to deprotonation for the acids except *o*-methylbenzoic acid, where it was paramagnetic and more appreciable than the diamagnetic shifts for the others (Table 3).

This and the absolute values of the signals for *o*-methylbenzoic acid and its complex mean that the methyl group was in a paramagnetically more shielded area. In the molecules having di-ortho, para, or di-ortho and para methyl groups, no significant differences were found in the magnetic behavior; i.e., the anisotropic paramagnetic shielding properties of the carbonyl group did not influence their chemical shifts. This is clear evidence that they are not in one plane.

## Conclusions

$Zn_4O$(carboxylate)$_6$ complexes could be synthesized without much difficulty using numerous alicyclic and aromatic carboxylic acids. It was found that the $Zn_4O$(1-adamantanecarboxylate)$_6$ and $Zn_4O$(1-adamantylacetate)$_6$ could be the best MOF precursors because of the size and rigidity of the linker and the many possibilities for substitution. Unfortunately, the complex formation could not go to completion because of the strong aggregation tendency of the ligand. There was no complex formation from phenylacetic acid and ZnO because of the high tendency of aggregation of the ligand. IR spectra indicated the loss of conjugation between the aromatic ring and the carboxylate group in di-*o*-methyl-substituted aromatic carboxylate ligands. The finding was verified and rationalized with molecular modeling and $^{1}$H and $^{13}$C NMR spectroscopies.

**Supporting Information Available:** Structures, spectra, parameters, and molecular modeling data. This material is available free of charge via the Internet at http://pubs.acs.org.