Syntheses, Crystal Structures and Thermal Behavior of Five New Complexes Containing 2,4,6-Trifluorobenzoate as Ligand

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In Memory of Professor Welf Bronger

Abstract. Five new complexes containing 2,4,6-trifluorobenzoate as ligand have been synthesized and structurally characterized, namely $Li(C_6F_3H_2COO)(H_2O)$ ($P2_1$, $Z = 2$, **1**), $Cs(C_6F_3H_2COO)(C_6F_3H_2COOH)$ ($P2_1/c$, $Z = 4$, **2**), $Cu(C_6F_3H_2COO)_2(H_2O)$ ($P\bar{1}$, $Z = 1$, **3**), $Cu(C_6F_3H_2COO)_2(MeOH)$ ($P2_1/c$, $Z = 4$, **4**) and $Ag(C_6F_3H_2COO)(H_2O)$ ($C2/c$, $Z = 8$, **5**). **1**–**3** and **5** are coordination polymers forming strands (**1**, **3**, **5**) or corrugated layers (**2**). In **1** and **2** the benzoate ligand acts as a bridging ligand, whereas in **3** and **5** the benzoate ligand is not bridging and the molecular units are interconnected by bridging water molecules. In **4** and **5**, dimeric Cu_2 and Ag_2 units, respectively, are formed with short M···M contacts. The dimeric units in **4** resemble the well-known paddlewheel structural motif. In **5** these dimeric units are further connected by bridging water molecules, whereas in **4** only very weak F···H interactions connect the dimeric units. DTA/TG experiments on **1**, **3** and **4** reveal that in a first step solvent molecules (H_2O, MeOH) are unquestionably released. In **1**–**5** the torsion angles of the carboxylate group with respect to the aromatic ring deviate significantly from zero. These results are in very good agreement with the results of quantum chemical calculations of free 2,4,6-trifluorobenzoic acid and its dimer at the DFT and RI-MP2 level of theory.

Dedicated Cluster

Introduction

The replacement of C–H by C–F entities in organic compounds leads to dramatic changes of their properties and reactivities. This aspect is well-known and well-established. But only recently, it was found that also in the field of coordination polymers (CPs) and metal-organic frameworks (MOFs) the use of fluorinated and perfluorinated bridging ligands may lead to materials with new or at least improved properties. So it was found that FMOF-1 shows a very high H_2 adsorption capacity.[1] This finding was corroborated by a theoretical investigation.[2] But in another work only a slightly enhanced H_2 adsorption capacity was reported[3] and *Klopper* et al. calculated an even lower H_2 adsorption enthalpy for fluorobenzene compared to unsubstituted benzene.[4] These discrepancies can simply be explained by the fact that for a long time no isostructural fluorous and non-fluorous compounds have been reported for a reliable experimental comparison of their adsorption properties. But very recently *Banerjee* et al. reported some isostructural porous coordination polymers and found that the H_2 uptake is "system-specific".[5] In a different approach focusing on the optical properties it was reported that CPs with perfluorinated ligands show a significantly enhanced luminescence.[6] In this context, we have started to investigate CPs with fluorinated and perfluorinated aromatic carboxylates as bridging ligands.[7–9] Indeed, we observed a bright luminescence in CPs of 4f-elements with tetrafluoroterephthalate as bridging ligand.[9] In this contribution we will report our investigations on compounds with 2,4,6-trifluorobenzoate as ligand. Although an efficient synthesis of 2,4,6-trifluorobenzoic acid[10,11] is known since 1970,[12] its crystal structure has only been reported very recently.[13] Even more surprisingly only two crystal structures of metal 2,4,6-trifluorobenzoates have been published up to now.[14,15] Both contain dimeric Ru_2 units with a paddlewheel-like arrangement of the trifluorobenzoate ligands. So the focus of this investigation is on the synthesis and structural characterization of 2,4,6-trifluorobenzoates with different metal ions and their thermal behavior. In the following, five new complexes will be presented.

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Results and Discussion

$Li(C_6F_3H_2COO)(H_2O)$ (1)

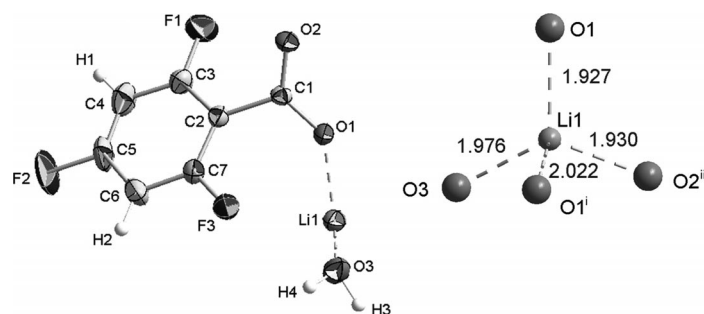Lithium-2,4,6-trifluorobenzoate·H_2O crystallizes in the acentric monoclinic space group $P2_1$ ($Z = 2$). The unit cell

Figure 1. Left: ORTEP plot (asymmetric unit) of $Li(C_6F_3H_2COO)(H_2O)$ (**1**) with labeling of atoms. Thermal ellipsoids are drawn at the 50 % probability level. Right: Tetrahedral coordination sphere of the lithium ion (O1^i: 2–x, 1/2+y, 1–z; O2^{ii}: x, 1+y, z).

parameters are a = 5.411(1) Å, b = 4.9795(9) Å, c = 14.775(3) Å, and β = 90.51(2)°. The asymmetric unit is shown in Figure 1 (left). Li$^+$ occupies the general position 2a and is coordinated by four oxygen atoms in a slightly distorted tetrahedral arrangement (Li–O: 1.927(4)–2.022(3) Å; O–Li–O: 94.64(13)–116.68(15)°, Figure 1 (right)). These oxygen atoms stem from the carboxylate groups of three trifluorobenzoate ligands (O1, O2) and one water molecule (O3). The carboxylate group of the 2,4,6-trifluorobenzoate ligand is μ_3-bridging with O1 coordinating to two Li$^+$ cations. The bridging nature of the carboxylate groups leads to strands of LiO$_4$ tetrahedra along [010] (Figure 2).

Figure 2. Strands of bridged LiO$_4$ tetrahedra along [010] in the crystal structure of $Li(C_6F_3H_2COO)(H_2O)$ (**1**). Hydrogen atoms of water molecules are omitted.

Weak O–H···O bonds (2.016(2) and 2.125(1) Å) connect these strands to layers in the (001) plane. These layers are further connected to a 3D structure by weak C–H···F (2.514(1)–2.535(2) Å) and O–H···F (2.723(1) Å) interactions.[16]

The DTA/TG diagram of **1** (Figure S2, Supporting Information) shows a broad endothermic weight loss of 9.0 % in the temperature range 110–150 °C, which corresponds to the release of one water molecule (calc.: 9.3 %). A sharp endothermic signal without any weight loss is observed at 250 °C. The nature of this signal is unclear, but it might be possible that a melting or a phase transition of anhydrous **1** occurs. In the temperature range 270–310 °C a weight loss of approx. 40 % is observed, which points to a decomposition of the ligand.

$Cs(C_6F_3H_2COO)(C_6F_3H_2COOH)$ (2)
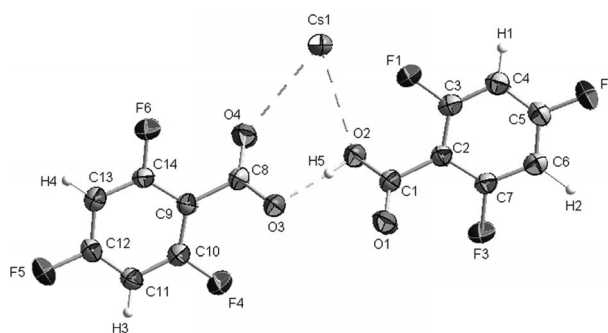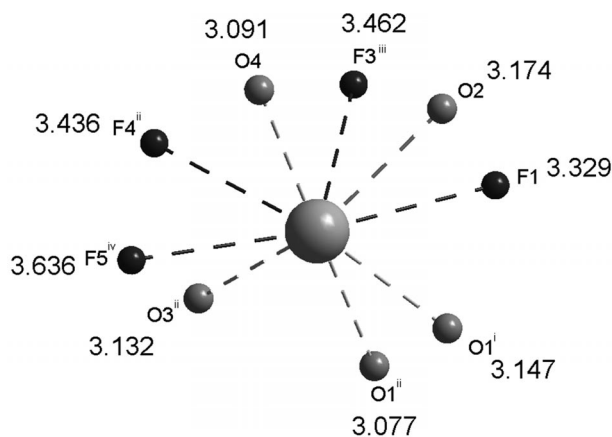
Cesium-2,4,6-trifluorobenzoate·$C_6F_3H_2COOH$ crystallizes in the monoclinic space group $P2_1/c$ (Z = 4) with a = 14.479(2) Å, b = 7.223(1) Å, c = 14.103(4) Å, and β = 90.07(2)°. The asymmetric unit is shown in Figure 3. It consists of one cesium cation, one trifluorobenzoate anion and one trifluorobenzoic acid molecule.

Figure 3. ORTEP plot (asymmetric unit) of $Cs(C_6F_3H_2COO)$-$(C_6F_3H_2COOH)$ (**2**) with labeling of atoms. Thermal ellipsoids are drawn at the 50 % probability level.

Cs$^+$ occupies the general position 4e and is surrounded by five oxygen atoms (O1^i, O1^{ii}, O2, O3^{ii} and O4). O1 and O2(H) stem from the acid molecule, whereas O3 and O4 constitute the carboxylate group of the anion. The bond lengths range from 3.077(4) Å (Cs1–O1^{ii}) to 3.174(3) Å (Cs1–O2). The -COOH group of the acid coordinates in a μ_3-bridging mode with O1 coordinating to two Cs$^+$ cations, whereas the benzoate anion coordinates in a μ_2-bidentate bridging mode. The coordination sphere of the Cs$^+$ cation with an unusual small coordination number (CN = 5) is completed by short Cs···F contacts. Four such contacts in the range 3.329(4) Å (Cs1–F1) to 3.636(3) Å (Cs1–F5^{iv}) are found as shown in Figure 4. Taking only Cs–O bonds into account, complex corrugated double-layers perpendicular to [100] are formed. These layers are obviously held together by weaker Cs···F interactions. Within the layers strong hydrogen bonds are found (O3···H5–O2: 1.65(9) Å),[16] which connect the anion and the acid molecule (Figure 3).

Figure 4. Coordination sphere of the cesium cation in Cs(C₆F₃H₂COO)(C₆F₃H₂COOH) (**2**); ^{i}: 1–x, –1/2+y, 1/2–z; ^{ii}: x, 3/2–y, –1/2+z; ^{iii}: 1–x, 1/2+y, 1/2–z; ^{iv}: –x, –1/2+y, 1/2–z.

Figure 6. Strands of edge-sharing CuO₆ octahedra along [100] in the crystal structure of Cu(C₆F₃H₂COO)₂(H₂O)₂ (**3**).

Cu(C₆F₃H₂COO)₂(H₂O)₂ (3)

Copper(II)-2,4,6-trifluorobenzoate·2H₂O crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$) with $a = 3.649(2)$ Å, $b = 6.421(3)$ Å, $c = 16.107(9)$ Å, $\alpha = 80.65(6)°$, $\beta = 84.50(6)°$, and $\gamma = 87.40(5)°$. The asymmetric unit is shown in Figure 5 (left). Cu²⁺ occupies the special position 1e and is coordinated octahedrally by six oxygen atoms (Figure 5, right), which belong to four water molecules (O3) and the carboxylate groups of two different benzoate ligands (O2). The second oxygen atom of the carboxylate group (O1) is non-coordinating, which leads to a significantly shorter C–O bond (C1–O1 = 1.235(5) Å vs. C1–O2 = 1.261(4) Å). The bond lengths within the CuO₆ octahedron range from 1.931(3) Å (Cu1–O2) to 2.667(3) Å (Cu1–O3). As expected for Cu²⁺ (3d⁹) a strong Jahn–Teller distortion is observed. Additionally, O–Cu–O angles close to 90° (89.2(1) and 90.8(1)°) are observed in the square planar CuO₄ plane, but the apices of the octahedron are significantly tilted (O3–Cu1–O3: 77.6(1) and 102.4(1)°, respectively).

Compared to **1** and **2**, the benzoate ligand in **3** is only unidentately bonded to copper and is thus not bridging the copper cations, which are interconnected via water molecules to form strands of edge sharing octahedra along [100] (Figure 6).

Within these strands strong hydrogen bonds are found: O1···H4–O3 = 1.68(9) Å. Weaker hydrogen bonds connect the strands to layers in the (001) plane: O1···H3–O3 = 2.01(6) Å. These layers are held together by weak interactions including H···F interactions starting at 2.521(3) Å.

The DTA/TG curve of **3** (Figure S5, Supporting Information) shows a continuous weight loss of approx. 13 % starting at 90 °C up to ca. 200 °C. This is much larger than the weight loss calculated for the release of two water molecules (8 %). Therefore it must be assumed that compound **3** already starts decomposing at these low temperatures. A further large weight loss is observed in the temperature range 220–260 °C (> 40 %). The remaining mass of approx. 30 % is larger than the calculated value for CuO (17.7 %).

Cu(C₆F₃H₂COO)₂(MeOH) (4)

Copper(II)-2,4,6-trifluorobenzoate·MeOH crystallizes in the monoclinic space group $P2_1/c$ ($Z = 2$) with $a = 7.665(1)$ Å, $b = 12.596(2)$ Å, $c = 17.206(3)$ Å, and $\beta = 84.50(6)°$. Cu²⁺ occupies the general position 4e. For Cu(C₆F₃H₂COO)₂ MeOH (**4**) the well-known paddlewheel structural motif is found

Figure 5. Left: ORTEP plot (asymmetric unit) of Cu(C₆F₃H₂COO)₂(H₂O)₂ (**3**) with labeling of atoms. Thermal ellipsoids are drawn at the 50 % probability level. Right: Coordination sphere of the Cu²⁺ cation in **3**; ^{i}: 1–x, 1–y, –z; ^{ii}: 2–x, 1–y, –z; ^{iii}: –1+x, y, z.

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(Figure 7), which was also reported for some Ru[II]-2,4,6-tri-fluorobenzoates[15] and Cu[II] acetate monohydrate.[17] Each copper dimer is bridged by four 2,4,6-trifluorobenzoate ligands (Cu–O: 1.941(4)–1.988(3) Å). The axial position is coordinated by the MeOH oxygen atom (Cu1–O5: 2.150(6) Å) and the Cu1–Cu1 distance within the dimer is 2.657(1) Å. All these distances are very close to those found in Cu[II] acetate monohydrate: $Cu–O_{bridging}$ = 1.945–1.994 Å, $Cu–O_{axial}$ = 2.156 Å and Cu–Cu = 2.616 Å. The paddlewheel units in **4** are held together by weak F⋯H interactions starting at 2.451(4) Å (F2⋯H4).
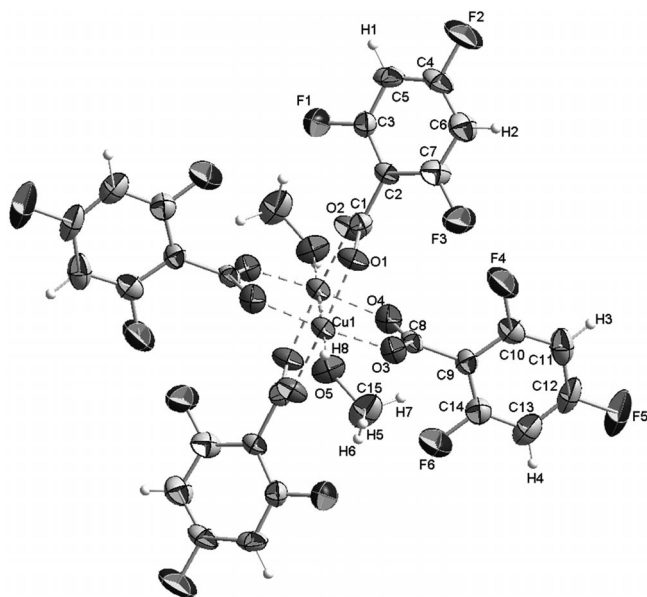
Figure 7. Paddlewheel structural motif in $Cu(C_6F_3H_2COO)_2·MeOH$ (**4**). The labeling of the atoms of the asymmetric unit is given. Thermal ellipsoids in the ORTEP plot are drawn at the 50% probability level.

It should be emphasized that one of the most famous MOFs (HKUST-1)[18] also contains a Cu_2 paddlewheel as characteristic structural building unit. Here the Cu_2 dimers are bridged by the carboxylate groups of trimesate anions (BTC[3−]), the axial positions are occupied by water molecules. As trimesate is a trifunctional ligand these paddlewheels are connected to form an open framework structure. The search for an analogous perfluorinated copper trimesate was unsuccessful up to now. So it is interesting to note that at least with monofunctional 2,4,6- trifluorobenzoate such a Cu_2 paddlewheel structural motif can be obtained.

The DTA/TG diagram (Figure S7, Supporting Information) shows a small endothermic weight loss of 2.5% at about 80 °C, which could not be assigned to any reasonable effect in **4**. So it might be interpreted as a hint for an impurity in the investigated sample (see: Experimental Section). In the temperature range 120–140 °C another endothermic weight loss of approx. 7.5% is observed. This agrees well with the calculated value for the loss of one coordinating methanol molecule (7.2%). A large weight loss of approx. 50% at 270 °C points to a decomposition of **4**. The remaining mass of approx. 40% is significantly larger than the calculated value for CuO (18%).
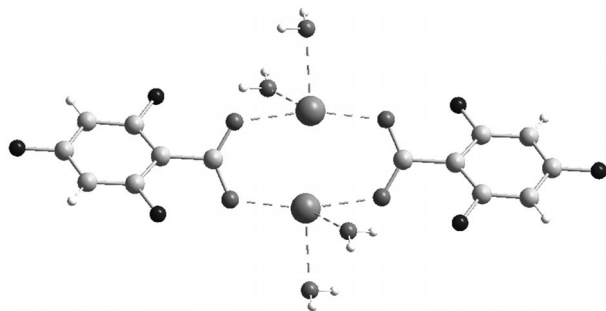
$Ag(C_6F_3H_2COO)(H_2O)$ (5)

Silver-2,4,6-trifluorobenzoate·H_2O crystallizes in the monoclinic space group $C2/c$ ($Z = 8$) with a = 32.405(7) Å, b = 3.6553(6) Å, c = 13.705(3) Å, and β = 90.67(2)°. The asymmetric unit is shown in Figure 8.
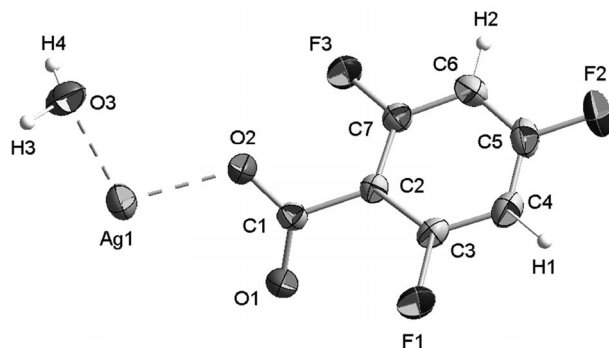
Figure 8. ORTEP plot (asymmetric unit) of $Ag(C_6F_3H_2COO)(H_2O)$ (**5**) with labeling of atoms. Thermal ellipsoids are drawn at the 50% probability level.

Ag^+ occupies the general position $8f$ and forms a dimeric Ag_2 unit (Ag–Ag: 2.819(1) Å). Each Ag^+ atom is coordinated by four oxygen atoms: two of them belong to bridging carboxylate groups (Ag1–O2: 2.196(3) Å; Ag1–O1: 2.212(3) Å) and two to water molecules (Ag1–O3: 2.455(4) Å; Ag1–O3: 2.803(4) Å). The O–Ag–O angles within the AgO_4 polyhedron deviate strongly from the ideal angle in a tetrahedron (109.5° vs. 70.2(1)–165.1(1)°). The dimeric unit is shown in Figure 9.

Figure 9. Dimeric unit in $Ag(C_6F_3H_2COO)(H_2O)$ (**5**).

These dimers are bridged through water molecules to form strands along [010]. These strands are held together by weak H⋯F interactions starting at 2.625(3) Å (H1⋯F2).

Theoretical Investigations

In most coordination compounds containing the benzoate anion as ligand an almost planar arrangement of the carboxylate group and the phenyl moiety is found (Figure 11). A survey of the Cambridge Structural Database (CSD)[19] shows that in more than 40% of the crystal structures containing benzencarboxylate anions a torsion angle between the carboxylate group and the phenyl ring in the range 0–10° is found. In contrast, for all compounds in this publication containing 2,4,6-trifluorobenzoate as ligand, a significant twist out of the plane of the

phenyl ring is observed (Table 1). This effect can be attributed to an electrostatic repulsion between the fluorine atoms on the ring and the oxygen atoms of the carboxylate groups as well as a decrease in aromatic character of the carboxylate group due to the electron-withdrawing nature of the fluorine atoms.[20,21]

Table 1. Torsion angles of the carboxylate group with respect to the phenyl moiety as found in the crystal structures of compounds **1–5** containing 2,4,6-trifluorobenzoate as ligand.

Li($C_6F_3H_2COO$)(H_2O) (**1**)	
C3–C2–C1–O2	41.5(2)°
C7–C2–C1–O2	–137.7(2)°
C3–C2–C1–O1	–137.8(2)°
C7–C2–C1–O1	43.0(2)°
Cs($C_6F_3H_2COO$)($C_6F_3H_2COOH$) (2)	
O1–C1–C2–C3	–129.3(5)°
O2–C1–C2–C3	50.4(6)°
O1–C1–C2–C7	46.3(6)°
O2–C1–C2–C7	–134.0(4)°
O4–C8–C9–C10	134.8(5)°
O3–C8–C9–C10	–46.8(6)°
O4–C8–C9–C14	–46.4(6)°
O3–C8–C9–C14	132.0(4)°
Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$ (3)	
O1–C1–C2–C3	–133.0(4)°
O2–C1–C2–C3	46.7(5)°
O1–C1–C2–C7	47.5(6)°
O2–C1–C2–C7	–132.8(3)°
Cu($C_6F_3H_2COO$)$_2$(MeOH) (4)	
C7–C2–C1–O2	–121.3(6)°
C3–C2–C1–O2	53.0(7)°
C7–C2–C1–O1	58.2(7)°
C3–C2–C1–O1	–127.5(5)°
C14–C9–C8–O4	–88.2(7)°
C10–C9–C8–O4	89.8(7)°
C14–C9–C8–O3	92.9(7)°
C10–C9–C8–O3	–89.0(6)°
Ag($C_6F_3H_2COO$)(H_2O) (5)	
O1–C1–C2–C3	137.0(4)°
O2–C1–C2–C3	–43.4(6)°
O1–C1–C2–C7	–41.9(6)°
O2–C1–C2–C7	137.7(4)°

In order to investigate the dihedral torsion of the carboxylate group with respect to the benzene plane in more detail, quantum chemical calculations were carried out on the respective acids. So the scope of the calculations was on both 2,4,6-trifluorobenzoic acid and benzoic acid; the investigation of the latter was done for benchmarking purposes. There are two possible orientations of the hydrogen atom of the carboxylate group in space. Those rotational conformations are illustrated in Figure 10. The computational investigation is based on geometry optimizations of both possible conformers of benzoic acid and 2,4,6-trifluorobenzoic acid in order to compare the dihedral angles of the optimized molecular structures. The dihedral angles are defined in terms of the atom labels as shown in Figure 10: $\alpha = \angle$(C4–C2–C1–O6), $\beta = \angle$(C4–C2–C1–O5), $\gamma = \angle$(C3–C2–C1–O6), and $\delta = \angle$(C3–C2–C1–O5).

The results of the calculations on benzoic acid are outlined in Table 2. The optimizations of conformer **I** show that the molecule is almost planar for the density functional methods as well as for the RI-MP2 method. This is in accordance with structural data of benzoates, where mainly planar anions are found (Figure 11). The optimized molecular structure of conformer **II** of benzoic acid yields a slightly out-of-plane tilted carboxylate group. The values for the dihedral angles range from –18.6° to –25.0°. But the relative energies of the compounds show that conformer **I** is the more stable one (5.5–6.3 kcal·mol^{-1}, Table S3 in the Supporting Information). The calculations of the dimers (Table S1, Supporting Information) yield planar molecular structures for the optimized DFT and RI-MP2 structures as well. The next step was to find the optimized geometries of 2,4,6-trifluorobenzoic acid. Here, the calculations on conformer **I** show a different picture: DFT calculations yield dihedral angles from ca. –39.0° to –43.1°. The optimizations within the RI-MP2 framework result in even higher dihedral torsion angles of ca. –46.4° to –49.1°. These values are similar to the dihedral angles calculated from the optimization of the dimers (Table S2, Supporting Information). For conformer **II** smaller torsion angles are calculated (Table
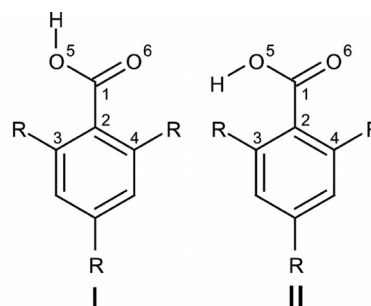
Figure 10. The two possible conformers of benzoic acid (R = H) and 2,4,6-trifluorobenzoic acid (R = F). For **I** the carboxylate-proton is orientated away from the phenyl moiety, for **II** the carboxylate-proton is pointing towards the substituent at the phenyl moiety.
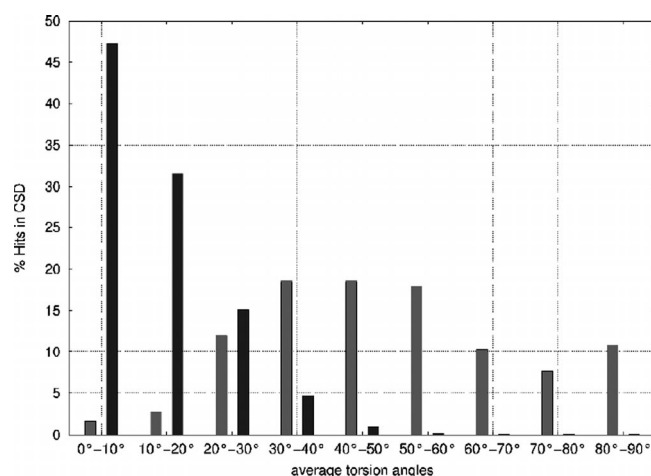
Figure 11. Torsion angles of the carboxylate group vs. the phenyl moiety of benzoates (dark grey) and 2,6-difluorobenzoates (light grey) as found in the Cambridge Structural Database (CSD).[19]

Table 2. Calculated dihedral angles for benzoic acid and its 2,4,6-fluorinated derivative.

benzoic acid						
Conf.	Method	Basis set	α	β	γ	δ
I	B3LYP	TZVP	0.3	−179.7	−179.7	0.3
I	RI-BP86	QZVP	0.4	−179.6	−179.6	0.4
I	RI-MP2	QZVP	0.0	−180.0	−180.0	0.0
II	B3LYP	TZVP	−20.5	159.4	158.1	−22.0
II	RI-BP86	QZVP	−18.6	161.1	160.3	−20.0
II	RI-MP2	QZVP	−23.8	156.0	155.2	−25.0
2,4,6-trifluorobenzoic acid						
Conf.	Method	Basis set	α	β	γ	δ
I	B3LYP	TZVP	−40.3	139.2	137.4	−43.1
I	RI-BP86	QZVP	−39.0	140.5	138.5	−42.0
I	RI-MP2	QZVP	131.6	−49.1	−46.4	132.9
II	B3LYP	TZVP	−23.4	155.9	154.0	−26.7
II	RI-BP86	QZVP	−18.4	161.0	159.7	−20.9
II	RI-MP2	QZVP	150.5	−30.4	−27.3	151.8

2), but it was found that conformer **II** is less stable than conformer **I** (Table S3, Supporting Information).

Despite this nice agreement between computational and experimental results it should be noted that the calculations were performed on the acids as optimized gas-phase structures. Solid state geometries of the anions should differ to these values. But nevertheless, the trend is clear: for unsubstituted benzoates and benzoic acid a planar conformation is preferred, whereas for fluorinated benzoates and benzoic acid a significant twist out of the plane of the phenyl moiety is found. Experimentally, results very similar to our observations in this contribution were found for 2,6-difluorobenzoates, as shown in Figure 11, as well as for tetrafluoroterephthalates.[8]

Conclusion

We have synthesized and structurally characterized five new complexes containing 2,4,6-trifluorobenzoate as ligand. In two compounds (Li($C_6F_3H_2COO$)(H_2O) (**1**) and Cs($C_6F_3H_2COO$)($C_6F_3H_2COOH$) (**2**)) the benzoate ligand acts as a bridging ligand so that coordination polymers with a 1D (**1**) and a 2D (**2**) structural motif are formed. In Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$ (**3**) and Ag($C_6F_3H_2COO$)(H_2O) (**5**) the benzoate ligand is not bridging and the molecular units are interconnected by bridging water molecules to form 1D structural motifs. Furthermore, in Cu($C_6F_3H_2COO$)$_2$MeOH (**4**) and **5**, dimeric Cu$_2$ and Ag$_2$ units with short M···M contacts are found. The dimeric units in **4** resemble the well-known paddlewheel structural motif that was also found in some Ru^{II}-2,4,6-trifluorbenzoates[15], Cu^{II} acetate monohydrate[17] and the MOF HKUST-1 with 1,3,5-benzenetricarboxylate as bridging ligand.[18] This seems to be quite remarkable, as a perfluorinated analogue of this MOF is still unknown. For comparable MOFs with 1,4-benzenedicarboxylate and its perfluorinated congeners as linkers it was argued that a twist of the carboxylate group out of the plane of the aromatic ring found in substituted systems is the reason that no isostructural perfluorinated MOFs can be found.[20] Actually, torsion angles in the range 53.0(7)–58.7(6)° are found in **4**, but the pad-

dlewheel motif is still formed. So we think that the search for isostructural perfluorinated MOFs is still worth the effort.

Experimental Section

Li($C_6F_3H_2COO$)(H_2O) (1): 2,4,6-trifluorobenzoic acid (100 mg, 0.57 mmol) and lithium acetate dihydrate (58 mg, 0.57 mmol) were dissolved in deionized water (20 mL). After slow evaporation of the solvent a precipitate was formed, from which single crystals of **1** were isolated. X-ray powder diffraction patterns (Figure S1 in the Supporting Information) confirm that the sample is single phase. Elemental analysis for Li($C_6F_3H_2COO$)(H_2O) (200.03 g·mol^{-1}): calcd. C 42.03 %, H 2.02 %; found C 42.93 %, H 1.92 %.

Cs($C_6F_3H_2COO$)($C_6F_3H_2COOH$) (2): 2,4,6-trifluorobenzoic acid (100 mg, 0.57 mmol) and cesium acetate (54.7 mg, 0.28 mmol) were dissolved in deionized water (20 mL). After slow evaporation of the solvent a precipitate was formed, from which a single crystal of **2** was isolated. Due to the fact that few single crystals were formed, only an X-ray powder diffraction pattern of **2** was recorded (Figure S3 in the Supporting Information) confirming the purity of the sample.

Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$ (3): 2,4,6-trifluorobenzoic acid (100 mg, 0.57 mmol) and copper acetate monohydrate (57 mg, 0.28 mmol) were dissolved in deionized water (20 mL). After slow evaporation of the solvent a precipitate was formed, from which blue single crystals of **3** were isolated. X-ray powder diffraction patterns (Figure S4 in the Supporting Information) confirm that the sample is single phase. Elemental analysis for Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$ (449.74 g·mol^{-1}): calcd. C, 37.39 %, H, 1.79 %, found C, 38.58 %, H, 2.38 %.

Cu($C_6F_3H_2COO$)$_2$(MeOH) (4): 2,4,6-trifluorobenzoic acid (100 mg, 0.57 mmol) and copper acetate monohydrate (57 mg, 0.28 mmol) were dissolved in methanol (20 mL). After slow evaporation of the solvent a precipitate was formed, from which turquoise single crystals of **4** were isolated. In the X-ray powder diffraction pattern (Figure S6 in the Supporting Information) a small amount of an unidentified impurity was observed. Elemental analysis for Cu($C_6F_3H_2COO$)$_2$(CH_3OH) (445.76 g·mol^{-1}): calcd. C, 40.42 %, H, 1.81 %, found C, 37.17 %, H, 1.71 %.

Ag($C_6F_3H_2COO$)(H_2O) (5): 2,4,6-trifluorobenzoic acid (100 mg, 0.57 mmol) and silver acetate (95 mg, 0.57 mmol) were dissolved in

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methanol (20 mL). After slow evaporation of the solvent a precipitate was formed, from which single crystals of **5** were isolated. In the X-ray powder diffraction pattern (Figure S8 in the Supporting Information) a large amount of an unidentified impurity was observed so that no further analytical investigations were performed.

Single Crystal Diffraction

Single crystals of **1–5** were isolated from the precipitates described above and measured with a Stoe IPDS I single crystal diffractometer ($T \approx 293$ K). The data collection and reduction was performed with the Stoe program package[22]. The crystal structures were solved by direct methods using SIR-92[23] or SIR-2004[24]. The structural models were completed using difference Fourier maps calculated with SHELXL-97,[25] which was also used for the refinements. All programs are part of the WINGX program suite.[26] For the refinements also SHELXLE[27], a frontend for SHELXL-97, was used. A numerical absorption correction was calculated and applied using X-Red[28] and X-Shape.[29] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms belonging to the 2,4,6-trifluorobenzoate ligand were refined "riding" with fixed C–H distances (0.93 Å). More details of the crystal structure solution and refinement are given in Table 3.

X-ray Powder Diffraction (XRPD)

XRPD patterns were recorded with a Huber G670 Guinier diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54051$ Å) with a Ge monochromator and an image plate detector. The patterns were measured as flat samples and are given in the Supporting Information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-884743 (Li($C_6F_3H_2COO$)(H_2O), **1**), CCDC-884744 (Cs($C_6F_3H_2COO$)($C_6F_3H_2COOH$), **2**), CCDC-884745 (Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$, **3**), CCDC-884746 (Cu($C_6F_3H_2COO$)$_2$-(MeOH), **4**), and CCDC-884747 (Ag($C_6F_3H_2COO$)(H_2O), **5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223-336-033; http://www.ccdc.cam.ac.uk/products/csd/request/].

Elemental Analysis

Elemental analyses were carried out with a CHNS Euro EA 3000 Analyzer (HEKAtech GmbH).

DTA/TG Measurements

DTA/TG measurements were performed with a NETZSCH STA 409 C using alumina crucibles in a constant argon stream (50 mL·min^{-1}). The heating rate was 15 K·min^{-1}. Sample masses were in the range 15–20 mg.

Quantum Chemical Calculations

The optimizations were carried out with the TURBOMOLE 6.3 program package[30] at different levels of theory. At first, standard density functional theory (DFT) was used for the geometry optimizations. The

Table 3. Crystal and structure refinement data for Li($C_6F_3H_2COO$)(H_2O) (**1**), Cs($C_6F_3H_2COO$)($C_6F_3H_2COOH$) (**2**), Cu($C_6F_3H_2COO$)$_2$(H_2O)$_2$ (**3**), Cu($C_6F_3H_2COO$)$_2$(MeOH) (**4**), and Ag($C_6F_3H_2COO$)(H_2O) (**5**).

	1	2	3	4	5
Molecular formula	$C_7H_4F_3LiO_3$	$C_{14}H_5CsF_6O_4$	$C_{14}H_8CuF_6O_6$	$C_{15}H_8CuF_6O_5$	$C_7H_4AgF_3O_3$
Formula weight /g·mol^{-1}	200.03	484.09	448.95	445.76	300.97
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$[a)]	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
T /K	293	293	293	293	293
a /Å	5.411(1)	14.479(2)	3.649(2)	7.665(1)	32.405(7)
b /Å	4.9795(9)	7.223(1)	6.421(3)	12.596(2)	3.6553(6)
c /Å	14.775(3)	14.104(2)	16.107(9)	17.206(3)	13.705(3)
α /°	90	90	80.65(6)	90	90
β /°	90.51(2)	90.07(2)	84.50(6)	101.68(2)	90.67(2)
γ /°	90	90	87.40(5)	90	90
V /Å^3	398.1(1)	1475.0(4)	370.5(3)	1626.9(4)	1623.3(6)
Z	2	4	1	4	8
D /g·cm^{-3}	1.67	2.18	2.00	1.82	2.46
Crystal size /mm	$0.3 \times 0.3 \times 0.1$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$
μ /mm^{-1}	– b)	2.599	1.578	1.433	– b)
Θ_{max} /°	28.2	28.2	28.2	28.2	28.1
Number of reflections					
measured	3804	13278	4453	15515	5497
independent	1804	3312	1645	3696	1938
Number of parameters	127	231	132	248	135
R-factors					
$I_o > 2\sigma(I_o)$	$R1 = 0.030$	$R1 = 0.047$	$R1 = 0.051$	$R1 = 0.045$	$R1 = 0.039$
	$wR2 = 0.062$	$wR2 = 0.130$	$wR2 = 0.124$	$wR2 = 0.074$	$wR2 = 0.096$
all data	$R1 = 0.048$	$R1 = 0.054$	$R1 = 0.072$	$R1 = 0.147$	$R1 = 0.058$
	$wR2 = 0.066$	$wR2 = 0.135$	$wR2 = 0.135$	$wR2 = 0.094$	$wR2 = 0.104$
R_{int}	0.050	0.078	0.084	0.164	0.038
GooF	0.942	1.045	1.022	0.736	1.042
$\Delta\rho_{min/max}$ /e·Å^{-3}	–0.148 / 0.158	–1.531 / 1.402	–0.518 / 1.686 c)	–0.872 / 0.591	–1.150 / 0.995

a) The absolute structure could not be determined, as **1** does not contain any heavy atoms. b) No absorption correction was applied. c) The high positive electron density is located on the special position 1a (000), 1.845 Å and 1.983 Å apart from the oxygen atoms O1 and O3.

chosen exchange-correlation functionals are the B3LYP hybrid functional[31–36] and the BP86 generalized-gradient approximation functional.[31,33,36,37] Besides density functional theory, second-order Møller–Plesset perturbation theory (RI-MP2)[38] was also used for the optimizations of the molecular structures. It was made use of the frozen-core approximation in the RI-MP2 method i.e. that the 1s orbitals of carbon, oxygen and fluorine were not correlated. Basis sets of different zeta qualities were used for the different methods. Among these are the def2-TZVP[39], def2-TZVPP[39] and def2-QZVP[40] basis sets. If the abbreviation of a method is preceded by the flag RI, the usage of the resolution of identity approximation[41] is implied. In these cases, the adequate auxiliary basis sets were employed.[42, 43]

Supporting Information (see footnote on the first page of this article): Experimental and simulated X-ray powder diffraction patterns of compounds **1**−**5**, DTA/TG diagrams of compounds **1**, **3**, **4** as well as tables containing dihedral angles of optimized geometries and relative energies (kcal·mol^{-1}) of both conformers of benzoic acid and 2,4,6-trifluoro benzoic acid.

Acknowledgment

References

[1] C. Yang, X. Wang, M. A. Omary, *J. Am. Chem. Soc.* **2007**, *129*, 15454.

[2] L. Zhang, Q. Wang, Y.-C. Liu, *J. Phys. Chem. B* **2007**, *111*, 4291.

[3] Z. Hulvey, D. A. Sava, J. Eckert, A. K. Cheetham, *Inorg. Chem.* **2011**, *50*, 403.

[4] O. Hübner, A. Glöss, M. Fichtner, W. J. Klopper, *J. Phys. Chem. A* **2004**, *108*, 3019.

[5] P. Pachfule, Y. Chen, J. Jiang, R. Banerjee, *Chem. Eur. J.* **2012**, *18*, 688.

[6] B. Chen, Y. Yang, F. Zapata, G. Qian, Y. Luo, J. Zhang, E. B. Lobkovsky, *Inorg. Chem.* **2006**, *45*, 8882.

[7] A. Orthaber, C. Seidel, F. Belaj, R. Pietschnig, U. Ruschewitz, *Inorg. Chem.* **2010**, *49*, 9350.

[8] C. Seidel, R. Ahlers, U. Ruschewitz, *Cryst. Growth Des.* **2011**, *11*, 5053.

[9] C. Seidel, C. Lorbeer, J. Cybińska, A.-V. Mudring, U. Ruschewitz, *Inorg. Chem.* **2012**, *51*, 4679.

[10] R. J. Harper, E. J. Soloski, C. Tamborski, *J. Org. Chem.* **1964**, *29*, 2385.

[11] R. J. de Pasquale, C. Tamborski, *J. Organomet. Chem.* **1968**, *13*, 273.

[12] S. Sugawara, N. Ishikawa, *Kogyo Kagaku Zasshi* **1970**, *73*, 972.

[13] R. Betz, T. Gerber, *Acta Crystallogr., Sect. E* **2011**, *67*, o539.

[14] Y. Sevryugina, B. Weaver, J. Hansen, J. Thompson, H. M. L. Davies, M. A. Petrukhina, *Organometallics* **2008**, *27*, 1750.

[15] H. Miyasaka, N. Motokawa, R. Atsuumi, H. Kamo, Y. Asai, M. Yamashita, *Dalton Trans.* **2011**, *40*, 673.

[16] G. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press New York, **1997**.

[17] P. de Meester, S. R. Fletcher, A. C. Skapski, *J. Chem. Soc., Dalton Trans.* **1973**, 2575.

[18] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[19] CSD Database, CCDC Cambridge (UK), Version: 5.33, Feb. **2012**.

[20] Z. Hulvey, J. D. Furman, S. A. Turner, M. Tang, A. K. Cheetham, *Cryst. Growth Des.* **2010**, *10*, 2041.

[21] Z. Wang, V. C. Kravtsov, R. B. Walsh, M. J. Zaworotko, *Cryst. Growth Des.* **2007**, *7*, 1154.

[22] *Stoe, IPDS Manual*; Stoe & Cie GmbH: Darmstadt, **2001**.

[23] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[24] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381.

[25] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

[26] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[27] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281.

[28] *X-Red*, Stoe & Cie GmbH: Darmstadt, **2001**.

[29] *X-Shape*, 1.06; Stoe & Cie GmbH: Darmstadt, **1999**.

[30] *Turbomole*, V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, **1989–2007**, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[31] J. C. Slater, *Phys. Rev.* **1951**, *82*, 538.

[32] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[33] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

[34] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.

[35] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[36] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[37] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[38] F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331.

[39] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[40] F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753.

[41] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283.

[42] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[43] A. Hellweg, C. Hättig, S. Höfener, W. Klopper, *Theor. Chem. Acc.* **2007**, *117*, 587.

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