

Basic Beryllium *ortho*-Fluorobenzoate and its Mono-hydroxo Derivative

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The preparation of tetraberyllium- μ_4 -oxo-hexa[η^2 -(*ortho*-fluorobenzoate)] [$\text{Be}_4\text{O}(\text{o-C}_6\text{H}_4\text{F-COO})_6$, **2**] and tetraberyllium- μ_4 -oxo- μ_2 -hydroxo-penta[η^2 -(*ortho*-fluorobenzoate)] [$\text{Be}_4\text{O}(\text{o-C}_6\text{H}_4\text{F-COO})_5(\text{OH})$, **3**] from silver *ortho*-fluorobenzoate and BeCl_2 in $\text{Et}_2\text{O}/\text{thf}$ solution containing varying amounts of water is reported. The single-crystal structures of **2**·tetrahydrofuran and **3**· Et_2O ·2 hexane are discussed in comparison with the structure of the known basic beryllium and zinc carboxylates [$\text{M}_4\text{O}(\text{RCOO})_6$, M = Be, Zn]. DFT calculations show that lower symmetry has to be expected for Be-based M_4O -framework-type compounds as compared to the corresponding Zn compounds. Compound **2** is a potential precursor for new compounds with MOF substructure motifs.

Key words: Beryllium, Cluster, Aryl-carboxylate, Crystal Structure

Introduction

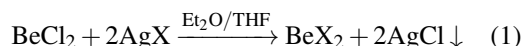
Some time ago we attempted the preparation of a crystalline compound with MOF-5 type structure [1] for polymeric beryllium-oxo-dicarboxylates obeying the ideal stoichiometry $\text{Be}_4\text{O}[\text{p-C}_6\text{H}_4(\text{CO}_2)_2]_3$ (**1**) [2]. Attempts to synthesize **1**, which is sometimes also referred to as Be-BDC (beryllium dicarboxylate), have been reported earlier [3] and very recently [4,5]. In both recent cases a micro-porous coordination polymer (MCP) was obtained. However, there are as yet no reports about the successful preparation of single-crystalline material of **1** suitable for X-ray diffraction studies.

In this work we report the finding of an unexpected and interesting side product stemming from attempts to prepare a binary stoichiometric beryllium carboxylate not containing oxide dianions.

This class of compounds is still a blank spot on the map of structurally well characterized inorganic compounds. However, our attempts did not yield the target compound but rather another unprecedented species which might offer access to a new type of MOF substructure compounds *via* condensation reactions with oligo carboxylic acids like terephthalic acid.

Results and Discussion

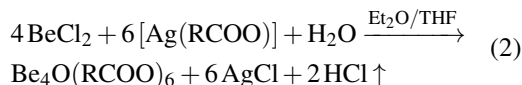
Commercially available, anhydrous beryllium dichloride is a convenient starting material for the preparation of beryllium coordination compounds, since it reacts exothermically with diethyl ether to form a soluble complex (forming a two-phase mixture of a solution of the complex in ether and a solution of ether in the complex) which for example readily undergoes salt metathesis reactions with silver salts:



Our attempts in preparing crystalline beryllium carboxylates of the stoichiometry $\text{Be}(\text{RCOO})_2$ according to Eq. 1 (with X = aryl-carboxylate), were not successful so far. However, a substoichiometric reaction yielding a compound of composition $\text{Cl}[\text{Be}(\mu_2\text{-RCOO})_3\text{Be}]\cdot\text{Et}_2\text{O}$, structurally related to binary zinc carboxylates, was observed (details are to be published elsewhere).

Led by the observation that small amounts of water, introduced by slightly moist solvents into reaction (2) (with X = RCOO), yield the well known oxide dianion-centered basic beryllium aryl-carboxylates

[Be₄O(RCOO)₆] (**2**), we tried to further explore this reaction type by using stoichiometric quantities of H₂O for R = *o*-C₆H₄F:

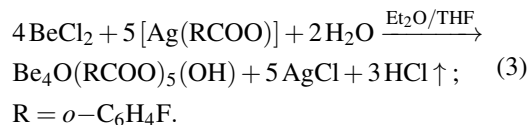


Single crystals suitable for X-ray diffraction were obtained by reducing the volume of the solution *in vacuo* followed by cooling to 3–5 °C.

Compound **2** crystallizes in the orthorhombic space group *Pbca*, with one stoichiometric equivalent of thf (see Fig. 1). Each unit cell comprises eight such formula units (*Z* = 8). There are no hints for other than van der Waals interactions between **2** and the thf molecule. There are no crystallographically imposed elements of symmetry within the molecules of **2**. In analogy to the other two structurally characterized basic beryllium-aryl carboxylates (*aryl* = phenyl, mesityl) [2], all six of the central O-Be-O-C-O-Be six-membered rings show significant deviations from planarity (hence the molecules cannot show higher symmetries than C₃, *vide infra*). The central Be₄O units show no large deviations from the tetrahedral geometry. All Be-O distances to the central oxygen atom O100 are in the range between 1.656(5) and 1.661(1) Å, the range defined by earlier reported analogous compounds [2]. The Be-O100-Be angles in the range from 106.3(3) to 110.8(3)° are showing no large deviations from the tetrahedral angle.

We tried to further investigate the effect of larger amounts of water on reaction (2). One of these

attempts, with R = *o*-C₆H₄F, led to the formation of the formerly unknown mixed beryllium-oxo-hydroxo/carboxylate Be₄O(RCOO)₅(OH) (**3**):



Single crystals suitable for X-ray diffraction could be obtained by layering the solution with hexane. It turned out that the structure of the product is closely related to the structure of tetraberyllium-oxo-hexacarboxylates, with one carboxylate group formally substituted by a hydroxy group.

Compound **3** crystallizes in the orthorhombic space group *Pnma*, with two stoichiometric equivalents of hexane and one of diethyl ether (the structure of **3** without solvent molecules is shown in Fig. 2). Each unit cell comprises four such formula units (*Z* = 4). Each diethyl ether molecule participates as an H-bond acceptor for the H atom of the bridging hydroxyl function, with an Et₂O...H distance of 1.83 Å. Apart from this, no other than van der Waals interactions could be detected between the molecules in the crystal. Each molecule of **3** possesses a crystallographically imposed mirror plane coinciding with the plane defined by the fluoro-phenyl unit with carbon atoms C11-C16 and bisecting the diethyl ether molecules. This molecular symmetry requires a complete planarity of the O1-Be3-O11-C10-O12-Be1 six-membered ring, a structural motif which is yet unprecedented in basic

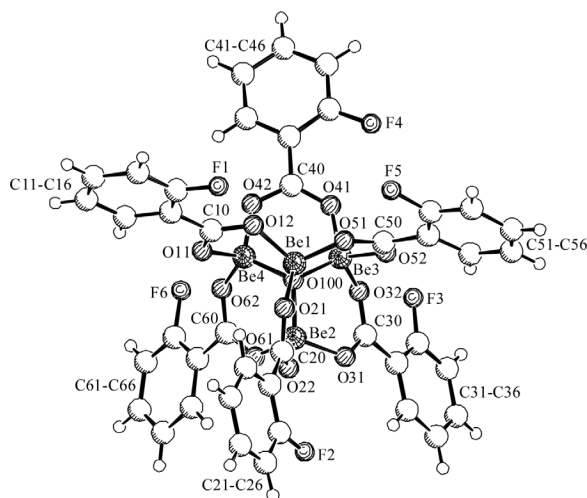


Fig. 1. Molecular structure of **2** in the crystal (SCHAKAL [11] plot). The thf molecule has been omitted for clarity.

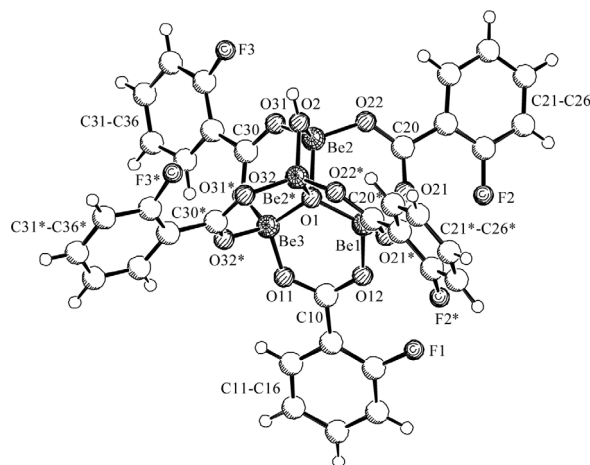


Fig. 2. Molecular structure of **3** in the crystal (SCHAKAL [11] plot). Et₂O and hexane molecules have been omitted for clarity.

beryllium-carboxylates. The existence of this mirror plane requires the Be2-O2-H and the Be2*-O2-H subunits to be equivalent by symmetry. The corresponding basic carboxylates of Be₄OR₆-type cannot possibly show mirror symmetry, due to the symmetry breaking *ortho*-substitution pattern of the phenyl ring replacing the hydroxy group. But also for un-substituted or symmetrically substituted organic groups such an arrangement appears unlikely since in all so far observed basic beryllium carboxylates substantial deviations from highly symmetrical configurations of the O_{center}-Be-O-C-O-Be six-membered ring units were observed, as outlined in [2] (see Fig. 9 therein) or [5].

This has been confirmed by DFT [RI-DFT(BP86)/SV(P)] calculations [6]. For isolated molecules, *T_d* symmetry is predicted for Zn₄O(O₂CH)₆ (**4**), but only C₃ for Be₄O(O₂CH)₆ (**5**).

All six-membered ring units C-O-Zn-O-Zn-O in **4** are calculated to be strictly planar while the C-O-Be-O-Be-O six-membered ring units in **5** show significant deviations from planarity (see Fig. 3).

One of the reasons for the deviations might be a certain misfit between the optimal acceptor sites of the relatively small Be₄O subunits compared to the Zn₄O subunits found in the analogous zinc compounds, and the positions of the lone pairs of electrons as provided by the rigid carboxylate groups.

This deviation from higher symmetry needs to be considered as the reason for the difficulties one faces in trying to synthesize macro-crystalline MOF-5 type compounds based on basic beryllium carboxylates. Ideally a perfectly octahedral arrangement of the organic substituents (or an affine transformation thereof),

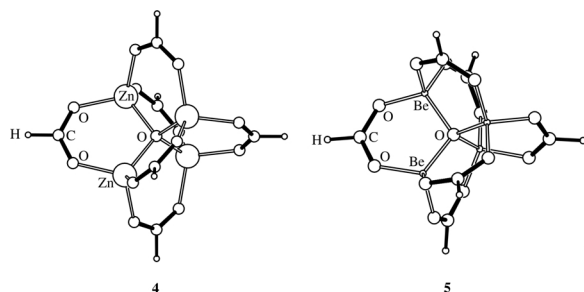


Fig. 3. DFT-optimized [6] molecular structures of (a) Zn₄O(O₂CH)₆ (**4**) and (b) Be₄O(O₂CH)₆ (**5**). While the six-membered ring units C-O-Zn-O-Zn-O in **4** are strictly planar, the C-O-Be-O-Be-O six-membered ring units in **5** show significant deviations from planarity. The C-H bonds are pointing at the vertices of an ideal octahedron in the case of **4**, while in the case of **5** there are significant deviations from the octahedral arrangement.

as it is found for analogous zinc compounds [4], is required [2, 4, 5].

In contrast to the known basic beryllium carboxylates [10], in **3** some significant deviations from the regular tetrahedral geometry in the central Be₄O moiety are also found. The Be2-O1 bond length from the central oxygen atom to the beryllium atoms connected to the bridging hydroxyl function is 1.584(5) Å, which is significantly shorter than the corresponding distances in the basic beryllium carboxylates, ranging from 1.652(2) to 1.668(5) Å [2]. These short Be-O distances are connected with a small Be2-O1-Be2* angle of 84.2(3)°. By contrast the opposing Be1-O1-Be3 angle of 115.1(3)° is considerably larger than the ideal tetrahedral angle of 109.5°. It is interesting to note that under these circumstances the Be1-O1 and Be3-O1 distances [1.617(6) and 1.607(6) Å] are also shorter than the corresponding ones in the basic beryllium carboxylates [1.652(2)–1.668(5) Å, see above]. This shortening of the Be-O distances is connected with the planar coordination geometry of the carboxylate group O11-C10-O12 with respect to the Be3-O1-Be1 moiety.

The spatial orientation of the fluorine atoms F3 and F3* might suggest an interaction with the hydrogen atom of the hydroxyl function. However, with a large distance of 4.168 Å between the F3 and H atoms, significant intramolecular interactions of hydrogen bond-type can be ruled out.

Given the different reactivities of carboxylate and hydroxo functions, there may be a possibility to selectively replace the hydroxo function by different carboxylate anions or – with two formula units – by one terephthalate dianion to yield MOF-5 substructure-type compounds. Some of us are currently investigating such possibilities using beryllium as well as zinc precursor compounds.

Experimental Section

Synthesis

All solvents were dried and distilled before use. Anhydrous, sublimed BeCl₂ was purchased from Sigma-Aldrich, and anhydrous silver *o*-fluorobenzoate Ag[*o*-C₆H₄F-COO] was prepared from an aqueous solution of K[*o*-C₆H₄F-COO] and AgNO₃ following a literature procedure [12].

Compound **2** was obtained from the reaction of a solution of 0.322 g (4.0 mmol) BeCl₂ in 15 mL of diethyl ether with a suspension of 1.580 g (6.0 mmol) Ag[*o*-C₆H₄F-COO] in 5 mL of thf. The suspension was added in small portions under continuous stirring using a dropping funnel equipped

Table 1. Crystallographic data and structure refinements of **2**·thf and **3**·hexane·2Et₂O.

Chemical formula	Be ₄ O(FH ₄ C ₆ CO ₂) ₆ ·C ₄ H ₈ O	Be ₄ O(OH)(FH ₄ C ₆ CO ₂) ₅ ·(C ₂ H ₅) ₂ O·2C ₆ H ₁₄
Empirical formula	C ₄₆ H ₃₂ Be ₄ F ₆ O ₁₄	C ₄₅ H ₄₅ Be ₄ F ₅ O ₁₃
<i>M_r</i>	958.76	924.85
Temperature, K	223(2)	223(2)
Wavelength, Å	1.54178	1.54178
Crystal system, space group	orthorhombic, <i>Pnma</i>	orthorhombic, <i>Pbca</i>
Unit cell dimensions		
<i>a</i> , Å	11.4208(2)	10.8817(4)
<i>b</i> , Å	20.4147(5)	16.0616(6)
<i>c</i> , Å	38.1008(8)	26.6560(11)
Volume, Å ³	8883.3(3)	4658.9(3)
<i>Z</i>	8	4
Calculated density, g cm ^{−3}	1.43	1.32
Absorption coefficient, mm ^{−1}	1.0	0.9
<i>F</i> (000), e	3920	1920
Crystal size, mm ³	0.55 × 0.15 × 0.02	0.20 × 0.15 × 0.06
Theta range, deg	2.32 to 68.00	4.39 to 68.09
Limiting indices	−13 ≤ <i>h</i> ≤ 13, −23 ≤ <i>k</i> ≤ 24, −45 ≤ <i>l</i> ≤ 45	−12 ≤ <i>h</i> ≤ 12, −19 ≤ <i>k</i> ≤ 19, −31 ≤ <i>l</i> ≤ 31
Reflections collected / unique	44140 / 7704	60161 / 4320
<i>R</i> _{int}	0.111	0.110
Completeness to $\theta = 68.00^\circ$, %	95.2	97.7
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9796 and 0.6005	0.9475 and 0.8392
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7704 / 0 / 671	4320 / 6 / 360
Goodness-of-fit on <i>F</i> ²	1.031	1.056
Final <i>R</i> ₁ / <i>wR</i> ² [<i>I</i> ≤ 2σ(<i>I</i>)]	0.0648 / 0.1420	0.0677 / 0.1630
Final <i>R</i> ₁ / <i>wR</i> ² (all data)	0.1215 / 0.1753	0.1043 / 0.1955
Largest diff. peak / hole, e Å ^{−3}	0.536 / −0.360	0.257 / −0.209
CCDC entry no.	842403	840884

with a magnetic stirrer designed by Woski [13]. After removing the funnel a 3.5 fold excess of water (0.2 mL, 4 mmol) was added with a syringe, and after further stirring of the reaction mixture for 2 h the resulting suspension was filtered using a syringe equipped with a Whatmann glass filter. The volume of the filtrate was reduced in a vacuum to about 15 mL, and the solution stored in the refrigerator at 3–5 °C. After 48 h clear colorless block-shaped crystals formed at the walls of the Schlenk flask. Single crystals suitable for X-ray diffraction were selected aided by a microscope equipped with a polarization filter.

Single crystals of **3**·hexane·2Et₂O were obtained from the reaction of a solution of 0.320 g (4.0 mmol) BeCl₂ in 15 mL of diethyl ether with a suspension of 1.581 g (6.0 mmol) Ag[*o*-C₆H₄F-COO] in 5 mL of thf which was not dried. The suspension was added in small portions under continuous stirring using a dropping funnel equipped with a magnetic stirrer designed by Woski [13]. After further stirring of the reaction mixture for 2 h, the resulting suspension was filtered using a syringe equipped with a Whatmann glass filter. The volume of the filtrate was reduced in a vacuum to about 15 mL. The resulting clear one-phase solution was covered with a layer of hexane and stored in the refrigerator at 3–5 °C. After 12 h clear colorless block shaped crys-

tals formed at the walls of the Schlenk flask. Single crystals suitable for X-ray diffraction were selected aided by a microscope equipped with a polarization filter.

Crystal structure determination

The data sets for the solvates of compounds **3** and **4** were collected with a Nonius KappaCCD diffractometer. Programs used were: COLLECT (Nonius B.V., 1998) for data collection, DENZO-SMN for data reduction [14], DENZO for absorption correction [15], SHELXS-97 for structure solution [16], and SHELXL-97 for structure refinement [17].

In the crystal structure of **3**·hexane·2Et₂O, in four of the six 2-fluorophenyl rings the fluorine atom can reside on the 2- or 6-position. Therefore the PART command was used to refine the ratio of occupation keeping the positions and thermal parameters of bonded phenyl carbon atoms the same. The ratios were refined to 0.802(7), 0.886(6), 0.625(6), and 0.900(6), respectively.

CCDC 840884 (**2**·thf) and 842403 (**3**·hexane·2Et₂O) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.com.ac.uk/data_request/cif.

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