Two Anhydrous Salts of Tetrafluoroterephthalic Acid (H₂tF-BDC): K₂tF-BDC and Rb₂tF-BDC

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Dedicated to Professor Bernt Krebs on the Occasion of His 75th Birthday

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Abstract. Two new anhydrous salts of tetrafluoroterephthalic acid (H₂tF-BDC), namely K₂tF-BDC (1) and Rb₂tF-BDC (2), were synthesized and structurally characterized. The crystal structure of 1 (*I*2/*m*, Z = 2) was solved and refined from X-ray single crystal data. K⁺ (CN = 8) is coordinated by six oxygen atoms of five different tF-BDC^{2–} linkers and two fluorine atoms of two of these linkers, which connect the KO₆F₂ polyhedra to a 3D network. The crystal structure of 2 ($P\bar{I}$, Z = 1) was refined from X-ray powder diffraction data. It crystallizes in a structure type already known from Tl₂tF-BDC. Rb⁺

Introduction

It is well-known that the replacement of C-H by C-F entities in organic compounds leads to dramatic changes of their properties and reactivity. Consequently, also in the field of coordination polymers (CPs) and metal-organic frameworks (MOFs) it has been attempted to adopt this finding by using fluorinated or perfluorinated bridging ligands for the synthesis of these compounds, as new or at least improved materials properties are expected. Indeed, it was found that FMOF-1 shows a high H₂ adsorption capacity.^[1] This result was corroborated by a theoretical investigation.^[2] But in another experimental work only a slightly enhanced H₂ adsorption capacity was reported^[3] and *Klopper* et al. calculated an even lower H₂ adsorption enthalpy for fluorobenzene compared to unsubstituted benzene.^[4] These discrepancies can simply be explained by the fact that no isostructural fluorous and non-fluorous compounds are compared and the influence of the specific crystal structure on the adsorption properties cannot be neglected. Accordingly, Banerjee et al. reported some isostructural porous coordination polymers with fluorinated and non-fluorinated ligands and found that the H₂ uptake is "sys-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201300480 or from the author. (CN = 8) is also coordinated by six oxygen and two fluorine atoms. But six tF-BDC²⁻ linkers are involved in the coordination. Again, a 3D network is formed. Both compounds can be obtained as single-phase samples. They are not porous and stable in air. The thermal stability was investigated by DTA/TG measurements. The decomposition starts at approx. 200 °C (1) and 230 °C (2). Their good solubility in water makes them interesting starting materials for the synthesis of new MOFs with the perfluorinated linker tF-BDC²⁻.

tem-specific".^[5] This finding is a little draw-back for the proposed high adsorption capacities of F-MOFs.

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.^[7-10] Indeed, we observed a bright luminescence in CPs of 4f elements with tetrafluoroterephthalate (tF-BDC²⁻) as bridging ligand.^[9,10] Obviously, the replacement of C-H by C-F entities reduces the C-H quenching significantly yielding CPs with quantum yields of up to 73% at room temperature.^[10] Unfortunately, for many systems the synthesis of CPs with tF-BDC²⁻ as linker is hampered by the fact that H₂tF-BDC only shows a very low solubility in water. This problem may be circumvented by using simple salts of H₂tF-BDC. But to the best of our knowledge, only (NH₄)₂tF-BDC has been described in the literature in more details.^[7] In this contribution we report the synthesis and crystal structure of two further simple salts of H₂tF-BDC, namely K₂tF-BDC (1) and Rb₂tF-BDC (2). Even more, 1 and 2 are two of the very few examples of solvent-free homoleptic coordination polymers with tF-BDC²⁻ as bridging ligand.

Results and Discussion

$K_2 tF - BDC (tF - BDC^{2-} = [p - (OOC)C_6 F_4(COO)]^{2-}) (1)$

Single crystals of K_2 tF-BDC (1) were synthesized by an evaporation method using a volatile base (see Experimental Section) starting from H₂tF-BDC and KCl. The sample is single-phase, as revealed by elemental analysis and X-ray powder

diffraction. **1** can also be obtained by a mechanochemical approach starting from H_2 tF-BDC and K(CH₃COO) (Experimental Section). But the powder diffractogram of the latter sample shows some weak impurity reflections, although the elemental analysis also points to a sample of high purity.

The crystal structure of **1** was solved and refined from X-ray single crystal data. **1** crystallizes in the monoclinic space group I2/m with Z = 2. The non-standard setting was chosen, as for the standard setting $C2/m \beta$ was larger than 120° . Selected crystallographic and refinement data are given in Table 1, some interatomic distances and angles are listed in Table 3. In Figure 1 the ORTEP plot of **1** is shown, where the numbering of the atoms of the asymmetric unit is given. K⁺ occupies the special position 4g, whereas the tF-BDC^{2–} anion is placed on the twofold axis (along C1–C2) with the mirror plane perpendicular to it. So the whole anion is generated from only five crystallographically distinct atoms (C1, C2, C3, F1, O1).

Table 1. Selected crystal and structure refinement data for K₂tF-BDC (1), X-ray single crystal data (STOE IPDS I, Mo- K_{α} radiation).

Molecular formula	$C_8F_4K_2O_4$
$M_{\rm r}$ /g·mol ⁻¹	314.283
Crystal system	monoclinic
Space group, Z	<i>I</i> 2/ <i>m</i> , 2
T/K	295
a /Å	4.0394(9)
b /Å	19.953(3)
c /Å	6.0480(13)
β /°	91.25(3)
V/Å ³	487.3(2)
$D/g \cdot cm^{-3}$	2.142
Crystal size /mm ³	$0.7 \times 0.4 \times 0.2$
μ / mm^{-1}	1.04
$\Theta_{\rm max}$ /°	28.2
Number of reflections	
measured	2937
independent	570 [464 with $I > 2\sigma(I)$]
Number of parameters	44
R-factors	
$I_{\rm o} > 2\sigma(I_{\rm o})$	$R_1 = 0.054$
	$wR_2 = 0.143$
All data	$R_1 = 0.061$
	$wR_2 = 0.147$
R _{int}	0.077
GooF	1.06
$\Delta \rho_{\min/\max}$ /e·Å ⁻³	-1.07 / 0.49

K⁺ is coordinated by six oxygen atoms of five different tF-BDC^{2–} ligands forming a distorted trigonal prism (Figure 4, left). K⁺ is located in the basal plane of the trigonal prism and its coordination is completed by two K···F contacts [2.840(2) Å] to two of the five coordinating ligands. The trigonal prism is formed by one chelating carboxylate group [K1–O1 = 2.852(3) Å, 2×] and four monodentately coordinating carboxylate groups [K1–O1 = 2.723(2) Å, 2× and 2.864(2) Å, 2×]. These distances are in reasonable agreement with the K–O distances found in ionic K₂O (K–O = 2.787 Å) ^[11] and somewhat longer than the K–F distances found in ionic KF (K–F = 2.672 Å)^[12]. In Cs(C₆F₃H₂COO)(C₆F₃H₂COOH)^[15] a similar trend was observed, i.e. Cs–O distances in the range



Figure 1. ORTEP plot of K_2 tF-BDC (1) with labelling of the atoms of the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level.



Figure 2. Projection of the crystal structure of K_2 tF-BDC (1) along [100]. KO₆ trigonal prisms as well as the unit cell are emphasized. K···F contacts are shown as dotted lines.

3.077(4) Å to 3.174(3) Å and only slightly larger Cs–F distances starting at 3.329(4) Å. The KO₆ trigonal prisms are connected by common edges with other KO₆ units thus forming layers perpendicular to the [010] direction. This is shown in Figure 2. Within these layers each K⁺ is surrounded by six K⁺ cations with distances ranging from 4.039 Å to 4.355 Å. This arrangement is not planar like in a hexagonal close packing, but strongly corrugated (see Figure 2). These layers of composition (KO₂)_∞ are connected by the tF-BDC^{2–} ligands to form a non-porous 3D network (Figure 2). Thereby, each K⁺ cation and each carboxylate group act as a 5-connector. The distances and angles within the tF-BDC^{2–} ligand are in the expected ranges. Only the torsion angle O1–C1–C2–C3 = 33.2(2)° is re-



markable, as it indicates that the carboxylate groups and the aromatic ring are not coplanar. But this has already been observed earlier^[7–10] and was attributed to the repulsion between the fluorine atoms of the ring and the oxygen atoms of the carboxylate groups.^[13,14] Calculations on 2,4,6-trifluoroben-zoates confirmed these large torsion angles.^[15]

$Rb_{2}tF$ -BDC (tF- $BDC^{2-} = [p$ -(OOC) $C_{6}F_{4}(COO)]^{2-}$) (2)

Attempts to synthesize single crystals of **2** suitable for a structural analysis failed. But a crystalline powder of reasonable quality was obtained by an evaporation method using a volatile base (see Experimental Section) starting from H_2tF -BDC and RbNO₃.

The crystal structure of **2** was refined from X-ray powder diffraction data (Figure 3), which also confirms that the sample is single-phase. Details are given in the Experimental Section. **2** crystallizes in a structure type that was found earlier for Tl₂tF-BDC ($P\bar{1}, Z = 1$).^[8] Selected crystallographic and refinement data are given in Table 2, some interatomic distances and angles are listed in Table 3. In Figure 4 (right) the coordination of the Rb⁺ cation is shown with the numbering of the atoms of the asymmetric unit. Rb⁺ as well as all atoms of the tF-BDC^{2–} ligand occupy the general position 2*i*. The center of the anion is located on a center of symmetry so that the whole anion is generated from eight crystallographically distinct atoms (C1, C2, C3, C4, F1, F2, O1, O2).



Figure 3. Rietveld refinement of X-ray powder diffraction data (293 K, STOE Stadi P, Cu- $K_{\alpha 1}$ radiation) of Rb₂tF-BDC (**2**). Experimental data points (+), calculated profile (solid line), and difference curve (below) are shown. Vertical bars mark the positions of Bragg reflections.

 Rb^+ is coordinated by six oxygen atoms of five different tF-BDC^{2–} ligands forming a polyhedron that might be described as a very distorted octahedron (Figure 4, right). Rb^+ is located in one of the trigonal faces of this octahedron and its coordination is completed by two Rb···F contacts [2.910(3) Å and 3.007(4) Å] to two tF-BDC^{2–} ligands. In contrast to 1 by these Rb···F contacts a sixth ligand is included in the coordination sphere of 2 (cp. Figure 4). The distorted octahedron is formed by one chelating carboxylate group [Rb1–O1 = 3.019(7) Å,

Table 2. Selected crystal and structure refinement data for Rb₂tF-BDC (2), X-ray powder diffraction data (STOE Stadi P, Cu- $K_{\alpha 1}$ radiation).

Molecular formula	$C_8F_4O_4Rb_2$
$\overline{M_{\rm r}}$ /g·mol ⁻¹	407.02
Crystal system	triclinic
Space group, Z	<i>P</i> 1, 1
T/K	293
a /Å	3.7562(1)
b /Å	6.6247(2)
c /Å	10.2326(4)
$a /^{\circ}$	106.792(3)
β /°	92.148(2)
γ /°	92.897(2)
$V/Å^3$	243.09(2)
D /g·cm ⁻³	2.780
R _p	0.028
wRp	0.037
R _{Bragg}	0.043
Data points	8251
No. of refined parameters	49
No. of restraints	16
No. of reflections	396
Background ^{a)}	9
Profile function	Pseudovoigt, ^[25] 2 coefficients
Data range	$7.5^\circ \le 2\theta \le 90^\circ$

a) No. of terms (linear interpolation function).

Table 3. Selected interatomic distances /Å and angles /° in K₂tF-BDC (1) and Rb₂tF-BDC (2).

K ₂ tF-BDC (1)		Rb_2tF -BDC (2)	
K1–O1 (2×)	2.723(2)	Rb1–O1	2.847(5)
K1–F1 $(2 \times)$	2.840(2)	Rb1–O2	2.868(7)
K1–O1 $(2 \times)$	2.852(3)	Rb1–F1	2.910(3)
K1–O1 (2×)	2.864(2)	Rb1–O1	2.954(7)
		Rb1–F2	3.007(4)
		Rb1–O1	3.019(7)
		Rb1–O2	3.020(7)
		Rb1–O2	3.052(7)
K1–K1 $(2 \times)$	4.0394(9)	Rb1–Rb1 $(2 \times)$	3.7562(1)
K1-K1 $(2 \times)$	4.293(1)	Rb1–Rb1	3.794(3)
$K1-K1 (2 \times)$	4.355(1)	Rb1–Rb1	4.040(3)
$C1-O1(2\times)$	1.252(3)	C1–O (2×)	1.25 ^{a)}
C1–C2	1.522(6)	C1–C2	1.52 ^{a)}
C2–C3 (2×)	1.393(4)	Carom-Carom	1.38 ^{a)}
C3–C3	1.379(6)		
C3-F1	1.343(3)	C _{arom} -F	1.34 ^{a)}
01-C1-O1	126.2(4)	O1C1O2	122.5(6)
$O1-C1-C2 (2 \times)$	116.9(2)	O1C1C2	120.0(6)
		O2-C1-C2	117.4(6)
O1-C1-C2-C3	33.2(2)	O1-C1-C2-C3	-40.2(2)
		O1-C1-C2-C3	139.1(2)
		O2-C1-C2-C3	-45.7(2)
		O2-C1-C2-C3	135.0(2)

a) Soft constraints.

Rb1–O2 = 3.052(7) Å] and four monodentately coordinating carboxylate groups [Rb1–O1 = 2.847(5) Å and 2.954(7) Å, Rb1–O2 = 2.868(7) Å and 3.020(7) Å]. These distances are in reasonable agreement with the Rb–O distances found in ionic Rb₂O (Rb–O = 2.925 Å)^[16] and somewhat longer than the Rb– F distances found in ionic RbF (Rb–F = 2.820 Å)^[17]. The RbO₆ polyhedra are connected by common edges with other RbO₆ units thus forming layers of composition (RbO₂)_∞, which



Figure 4. Coordination spheres around K^+ in **1** (left) and around Rb^+ in **2** (right). $K \cdots F / Rb \cdots F$ contacts are shown as dotted lines. For **2** the labelling of the atoms of the asymmetric unit is given.



Figure 5. Projection of the crystal structure of $Rb_2tF-BDC$ (2) along [010]. RbO₆ polyhedra as well as the unit cell are emphasized. Rb···F contacts are shown as dotted lines.

are shown in Figure 5. In contrast to 1 within these layers each Rb⁺ is surrounded by four Rb⁺ cations – instead of six neighboring K⁺ ions in 1 – with distances ranging from 3.7562 Å to 4.040 Å. Like in 1 this arrangement is not planar, but strongly corrugated (Figure 5). These $(RbO_2)_{\infty}$ layers are connected by the tF-BDC^{2–} ligands to form a non-porous 3D network (Figure 5). Including all Rb···O and Rb···F contacts each Rb⁺ cation and each side of the linker – including the carboxylate and C–F groups – act as a 6-connector. The distances and angles within the tF-BDC^{2–} ligand were constrained in the refinement of the XRPD data using values obtained from the single crystal structure analysis of 1 (for details see Experimental Section). However, the torsion angles between the carboxylate groups

and the aromatic ring were refined freely. Like in **1** torsion angles between 40.2° and 45.7° (Table 3) indicate that the carboxylate groups and the aromatic ring are not coplanar due to the repulsion between the fluorine atoms of the ring and the oxygen atoms of the carboxylate groups.^[13,14]

Thermal Properties

Compounds 1 and 2 show good solubility in water. Both are stable in air, an uptake of water was not observed. The thermal behavior of 1 (Figure S4, Supporting Information) and 2 (Figure S5, Supporting Information) was investigated by DTA/TG measurements. In an inert atmosphere a slow decomposition starts at approx. 200 °C (1) and 230 °C (2), respectively. The exothermic maximum is reached at 350 °C (1) and 370 °C (2). The decomposition seems to occur in at least two steps. For the release of two CO₂ molecules a mass loss of 28 % (1) and 21.6% (2) is calculated. Thus, a more complex decomposition than a simple decarboxylation must occur. The remaining masses at 600 °C are 35 % (1) and 41 % (2) being in the range of the possible residues K₂O ($m_{calc} = 30$ %), 2×KF ($m_{calc} = 37$ %), Rb₂O ($m_{calc} = 46$ %) and 2×RbF ($m_{calc} = 51$ %).

Conclusions

We have synthesized and structurally characterized two new anhydrous salts of tetrafluoroterephthalic acid (H₂tF-BDC), namely K₂tF-BDC (1) and Rb₂tF-BDC (2). Both can be classified as coordination polymers, as (K/RbO₂)_∞ layers are connected by the tF-BDC²⁻ ligand to form a non-porous 3D network. 1 and 2 are two of the very few examples of a homoleptic solvent-free coordination polymer of H₂tF-BDC. To the best of our knowledge only Tl₂tF-BDC, which was also synthesized and characterized in our group,^[8] has been reported up to now. Compound 2 crystallizes in the same structure type as Tl₂tF-BDC ($P\bar{1}$, Z = 1). The crystal structure of 1 (I2/m, Z = 2) is similar to that of 2, but shows some significant differences. In 1 a slightly distorted KO₆ trigonal prism is found with K⁺ located in one of the rectangular faces of this polyhedron. In 2, however a heavily distorted RbO_6 octahedron is formed with Rb⁺ located in one of the trigonal faces. In both crystal structures the coordination spheres are completed by two K···F and Rb···F contacts, respectively. In 1, however K⁺ acts as a 5-connector, whereas Rb⁺ in 2 acts as a 6-connector.

Both compounds 1 and 2 show a good solubility in water, which makes them interesting starting materials for the synthesis of new MOFs with the perfluorinated linker tF-BDC^{2–}. At the moment we are exploring the field of solvent-free homoleptic tetrafluoroterephthalates in more detail with respect to their luminescent properties^[6,9,10] as well as possible porous representatives.

Experimental Section

 $\rm H_2tF\text{-}BDC$ was synthesized according to the procedure described in the literature. $^{[7]}$



K₂[*p*-(**OOC**)C₆**F**₄(**COO**)] (1): (a) KCl (16.4 mg, 0.2 mmol) and H₂tf-BDC (23.8 mg, 0.1 mmol) were dissolved in EtOH/H₂O (1 mL, 1:1, v:v). In an open vial this solution was placed in a desiccator, whose bottom was filled with EtOH/DMF (100 mL, 3:1, v:v). A beaker with EtOH/DMF (40 mL, 3:1, v:v) and triethylamine (40 mL) was also placed in the desiccator, which was closed afterwards. After four weeks colorless single crystalline blocks of 1 were obtained, from which a single crystal suitable for a single crystal structure analysis was isolated. The resulting XRPD pattern and IR spectrum are given in the Supporting Information (Figures S1 and S3). Both as well as the elemental analysis indicate a single-phase sample. Elemental analysis for K₂(C₈F₄O₄) (314.28 g·mol⁻¹): calcd. C 30.57, H 0%; found C 30.50, H 0%.

(b) K(CH₃COO) (196.3 mg, 2 mmol) and H₂tf-BDC (238.3 mg, 1 mmol) were ground in an agate mortar by adding distilled water (50 μ L). After the smell of acetic acid was no longer noticed, the resulting product was dried in vacuo. The resulting XRPD pattern is given in the Supporting Information (Figure S2). Some weak extra reflections indicate a small amount of an unknown impurity. The elemental analysis however does not indicate any impurities. Elemental analysis for K₂(C₈F₄O₄) (314.28 g·mol⁻¹): calcd. C 30.57, H 0%; found C 30.68, H 0%.

Rb₂[*p*-(**OOC**)C₆F₄(**COO**)] (2): RbNO₃ (29.5 mg, 0.02 mmol) and H₂tf-BDC (24 mg, 0.01 mmol) were dissolved in EtOH/DMF (1.5 mL, 3:1, v:v) and filled into a small vial, which was closed with a perforated foil. The vial was placed in a snap cap tube, which had been filled with EtOH/DMF (4 mL, 3:1, v:v) and triethylamine (3:1, v:v) before. After two weeks colorless single crystals of **2** were obtained, which were used to determine the unit cell of **2**, but the quality did not allow a complete single crystal structure analysis. These crystals were ground to a fine powder, which was used for the final structure analysis and refinement (Figure 3).

Single Crystal Diffraction: A single crystal of **1** was isolated from the precipitate described above and measured with a Stoe IPDS I single crystal diffractometer ($T \approx 295$ K). Data collection and reduction was performed with the Stoe program package.^[18] The crystal structure was solved by direct methods using SIR-92.^[19] The structural models were completed using difference Fourier maps calculated with SHELXL-97,^[20] which was also used for the refinements. All programs are part of the WINGX program suite.^[21] A numerical absorption correction was applied using X-Red^[22] and X-Shape.^[23] All atoms were refined anisotropically. More details of the crystal structure solution and refinement are given in Table 1.

X-ray Powder Diffraction (XRPD): XRPD patterns were recorded with a STOE Stadi P diffractometer with Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.54051$ Å) using a Ge monochromator and a PSD detector. Samples of **1** were measured as flat samples, whereas a sample of **2** was placed in a capillary ($\emptyset = 0.3$ mm). Samples are typically measured for 90 min with a step size $2\theta = 0.01^{\circ}$. To improve the quality of the XRPD data of **2** several of such measurements were added.

As the unit cell of **2** could be determined from a single crystal (see above), it was already concluded from this unit cell that **2** crystallizes in the Tl₂tF-BDC type structure.^[8] The final refinement of the crystal structure of **2** was performed on the X-ray powder diffraction data (Figure 3) using the Rietveld method.^[24] The atomic coordinates of Tl₂tF-BDC were used as starting parameters. The following soft constraints for the tF-BDC^{2–} linker were used to obtain a stable and converging refinement: C–F = 1.34(1) Å, C–O = 1.25(1) Å, C_{arom}–C_{arom} = 1.38(1) Å, and C1–C2 = 1.52(1) Å. All C–C–C and F–C–C angles

of neighboring atoms were set to $120(1)^{\circ}$. The atoms O1, O2, C1, C2 as well as the atoms C1, C2, C3, C4, F1, F2 were defined as planar units. Finally, the U_{iso} s of O1 and O2 as well as those of C1, C2, C3, C4, F1, F2 were constrained. The quality of the data and the refinement can be estimated from Figure 3. Some crystallographic and refinement data are summarized in Table 2.

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

IR Spectroscopy: FT-IR measurements were carried out on solid KBr pellets with a Bruker ALPHA-T spectrometer.

DTA/TG Measurements: DTA/TG measurements were performed with a Perkin-Elmer STA 6000 using alumina crucibles in a constant argon stream (20 mL·min⁻¹). The heating rate was 10 K·min⁻¹. Sample masses were 7.2 mg (1) and 2.5 mg (2).

Supporting Information (see footnote on the first page of this article): Experimental and simulated X-ray powder diffraction patterns, IR spectrum, and DTA/TG diagram of compounds **1** and **2**.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-959837 (1) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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ARTICLE

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