[Li₂(tF-BDC)(DMF)₂]: A New Alkali Metal Salt of Tetrafluoroterephthalic Acid (H₂tF-BDC)

Benedikt Dolfus^[a] and Uwe Ruschewitz^{*[a]}

Dedicated to Professor Gerd Meyer on the Occasion of His 65th Birthday

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Abstract. The DMF solvate of lithium tetrafluoroterephthalate $[Li_2(tF-BDC)(DMF)_2]$ (H₂tF-BDC = tetrafluoroterephthalic acid) was synthesized and structurally characterized from X-ray single crystal data (*Pbcn*, Z = 8). Li⁺ (CN = 4) is coordinated tetrahedrally by four oxygen atoms of three different tF-BDC²⁻ linkers and one DMF molecule. The LiO₄ tetrahedra are connected by common vertices to chains, which are bridged by tF-BDC²⁻ linkers to form a 2D polymeric unit. The DMF molecules are oriented perpendicular to these polymeric sheets, which are stacked along [100] in an AB fashion and held together by weak van der Waals interactions. Single crystals of

Introduction

Coordination polymers (CPs) and porous metal-organic frameworks (MOFs) with fluorinated or perfluorinated linker ligands are supposed to show improved properties compared with their non-fluorinated congeners.^[1] Consequently, a high H₂ adsorption capacity was found for porous FMOF-1.^[2] This result was corroborated by a theoretical investigation,^[3] but in another experimental work only a slightly enhanced H₂ adsorption capacity was reported.^[4] Banerjee et al. showed for some isostructural porous coordination polymers with fluorinated and non-fluorinated ligands that the H₂ uptake is "system-specific",^[5] i.e. the influence of the crystal structure on the adsorption properties cannot be neglected. In this respect, it is interesting to note that isostructural fluorinated congeners of the well-known MOFs, MOF-5^[6] and MIL-53,^[7] are still unknown. In both terephthalate (1,4-benzenedicarboxylate = BDC²⁻) is incorporated as linking ligand. Despite the fact that its perfluorinated counterpart tetrafluoroterephthalate (tF-BDC²⁻) is commercially available and convenient syntheses have been reported in the literature,^[8,9] no isostructural or even porous homoleptic MOF with tF-BDC2- has been re[Li₂(tF-BDC)(DMF)₂] were synthesized by precipitation from an ethanol/DMF solvent mixture, but single-phase samples were only obtained by a mechanochemical approach starting from lithium acetate and H2tF-BDC by adding DMF. The thermal stability of [Li₂(tF-BDC)(DMF)₂] was investigated by DTA/TG measurements. The (endothermic) decomposition starts at 170 °C and is followed by a second exothermic decomposition at approx. 300 °C. The weight losses are in good agreement with a release of DMF and CO₂. LiF is identified in the residue after heating at 500 °C.

ported up to now. Obviously, the synthetic procedures for nonfluorinated MOFs cannot simply be transferred to their fluorinated congeners.

In a different approach focusing on the optical properties it was reported that CPs with perfluorinated ligands show a significantly enhanced luminescence.^[10] In this context, we observed a bright luminescence in CPs of 4f elements with tetrafluoroterephthalate (tF-BDC²⁻) as bridging ligand.^[11] Obviously, the replacement of C-H by C-F entities reduces the quenching of luminescent properties by C-H vibrations significantly. Unfortunately, the synthesis of CPs with tF-BDC²⁻ as linker is sometimes hampered by the low solubility of H₂tF-BDC in some solvents. This problem might be circumvented by using salts of H₂tF-BDC. Therefore, we have started to investigate salts of H₂tF-BDC in more detail and described the synthesis and structural characterization of anhydrous $M_{2}^{I}(\text{F-BDC})$ with $M^{I} = \text{NH}_{4}^{+,[9]} \text{K}^{+,[12]}$ and $\text{Rb}^{+,[12]}$ In this contribution we will report another example, namely [Li₂(tF-BDC)(DMF)₂].

Results and Discussion

Single crystals of [Li₂(tF-BDC)(DMF)₂] precipitated from a solution of LiCl·H₂O and H₂tF-BDC (tetrafluoroterephthalic acid) in EtOH/DMF (3:1, v:v), in which triethylamine was slowly diffused. A single crystal suitable for an X-ray single crystal structure analysis was isolated from this precipitate, but elemental analysis as well as X-ray powder diffraction (Figure S1, Supporting Information) revealed that the sample is not single-phase. Therefore, a mechanochemical synthesis was de-

^{*} Prof. Dr. U. Ruschewitz Fax: +49-221-470-3933

E-Mail: Uwe.Ruschewitz@uni-koeln.de

[[]a] Department für Chemie

Universität zu Köln Greinstraße 6 50939 Köln, Germany

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veloped, in which Li(CH₃COO)·2H₂O and H₂tF-BDC were carefully ground while adding DMF. Elemental analysis as well as X-ray powder diffraction (Figure S2, Supporting Information) confirmed that a single-phase sample was obtained.

[Li₂(tF-BDC)(DMF)₂] crystallizes in the orthorhombic space group *Pbcn* with Z = 8. The asymmetric unit consists of two symmetry independent Li⁺ cations, one tF-BDC²⁻ anion, and two symmetry independent DMF molecules (Figure 1). Each Li⁺ cation is coordinated by four oxygen atoms stemming from three different tF-BDC²⁻ anions and one DMF molecule. The Li-O distances range from 1.916(6) Å (O201) to 1.986(7) Å (O200) for Li50 and from 1.912(6) Å (O203) to 1.992(6) Å (O200) for Li51. No Li-F contacts shorter than 3 Å are found. The O-Li-O angles within the coordination polyhedra range from 100.7(4)° to 118.2(3)° for Li50 and from $103.8(3)^{\circ}$ to $114.5(3)^{\circ}$ for Li51. Thus, the values are close to the ideal value for a tetrahedron. Both DMF molecules show a strong disorder, which is reflected in somewhat unusual bonding distances and angles within the molecules as well as large thermal ellipsoids (Figure 1, see also Experimental Section). The distances and angles within the tF-BDC²⁻ anion are in the expected range. The carboxylate groups are tilted $[71.6(3)^{\circ}$ and $89.3(3)^{\circ}]$ with respect to the plane of the benzene ring like in many fluorinated benzenedicarboxylates. The reasons have already been discussed elsewhere.^[13]



Figure 1. ORTEP plot of $[Li_2(tF-BDC)(DMF)_2]$ with labelling of the atoms of the asymmetric unit. Thermal ellipsoids are drawn at the 30% probability level.

The LiO₄ tetrahedra in [Li₂(tF-BDC)(DMF)₂] are connected by common vertices involving oxygen atoms O200 and O202 of the carboxylate groups to form chains along [010]. These chains are linked by tF-BDC^{2–} anions to form a layer-like polymeric structural unit (Figure 2). The DMF molecules are oriented almost perpendicular to these layers, which are stacked along [100] in an AB fashion and held together by weak van der Waals interactions. In solvent-free M^{I}_{2} (tF-BDC) ($M^{I} = K^{+}$, Rb⁺) 3D networks have been found.^[12]



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Figure 2. View of the 2D polymeric unit in $[Li_2(tF-BDC)(DMF)_2]$ in a projection along [100]. LiO₄ tetrahedra are emphasized.

The thermal stability of [Li₂(tF-BDC)(DMF)₂] was investigated by a DTA/TG measurement in the range of 25-500 °C in an argon atmosphere (Figure S6, Supporting Information). An endothermic signal starting at approx. 170 °C (mass loss: ca. 26%) and a strong exothermic signal starting above 300 °C (mass loss: ca. 28%) were observed. For the release of one DMF molecule a theoretical value of 18.5% and for one CO₂ molecule 11.1 % are calculated. So for the release of two DMF and two CO₂ molecules a remaining mass of 40.8% is expected, which is in very good agreement with the mass obtained above 330 °C. Accordingly, in the residue after heating to 500 °C LiF was identified (Figure S7, Supporting Information) next to unidentified amorphous components. Heating [Li₂(tF-BDC)(DMF)₂] to 195 °C and 260 °C resulted in polycrystalline materials, which show significant changes of their XRPD patterns (Figure S8, Supporting Information). But the modest quality of the patterns did not allow a further elucidation of their crystal structures.

Conclusions

We have synthesized and structurally characterized the first lithium salt of tetrafluoroterephthalate, which crystallizes as a DMF solvate. Its crystal structure consists of layered polymeric structural units. A single-phase sample was obtained by grinding Li(CH₃COO) and H₂tF-BDC under DMF. The weaker acid (acetic acid) is released. This mechanochemical approach emerges as an interesting synthetic approach for the synthesis of new tetrafluoroterephthalates. The crystallinity of the samples obtained is surprisingly high (Figure S2, Supporting Information). However, single crystals could only be obtained by crystallization from a EtOH/DMF solvent mixture. Currently, we are investigating the potential of $[Li_2(tF-BDC)(DMF)_2]$ as starting material for the synthesis of new coordination polymers with tetrafluoroterephthalate as linker.

Experimental Section

 H_2 tF-BDC was synthesized according to the procedure described in the literature.^[9] Its purity was checked by NMR and X-ray powder diffraction (Figure S3, Supporting Information).

[Li₂(tF-BDC)(DMF)₂]: (a) LiCl·H₂O (12.1 mg, 0.02 mmol) and H₂tF-BDC (23.4 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 (Figure S4, Supporting Information). After 5 d, colorless needle-like single crystal structure analysis was isolated. The resulting XRPD pattern and IR spectrum are given in the Supporting Information (Figures S1 and S5). Both as well as the elemental analysis indicate that no single-phase sample was obtained. Elemental analysis for Li₂C₁₄F₄O₆H₁₄N₂ (396.15 g·mol⁻¹): calcd. C 42.45, H 3.56, N 7.07%; found C 37.27, H 4.07, N 2.87%.

(b) Li(CH₃COO)·2H₂O (306 mg, 3 mmol) and H₂tF-BDC (357 mg, 1.5 mmol) were ground in an agate mortar, while DMF (100 μ L) was added. 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). No impurity reflections were detected and the elemental analysis also indicates that a single-phase sample was obtained. This sample was used for the DTA/TG measurement. Elemental analysis for Li₂C₁₄F₄O₆H₁₄N₂ (396.15 g·mol⁻¹): calcd. C 42.45, H 3.56, N 7.07%; found C 41.24, H 3.78, N 6.58 %.

Single Crystal Diffraction: A single crystal of [Li₂(tF-BDC)(DMF)₂] was isolated from the precipitate of synthesis (a) and measured with a Stoe IPDS I single crystal diffractometer ($T \approx 20$ °C). Data collection and reduction were performed with the Stoe program package.^[14] The crystal structure was solved by direct methods using SIR-92.^[15] The structural models were completed using difference Fourier maps calculated with SHELXL-97,^[16] which was also used for the refinements. No absorption correction was applied. Hydrogen atoms were placed on calculated positions and refined with a "riding" model. All nonhydrogen atoms were refined anisotropically with the exception of C212. The methyl groups of both DMF molecules show a high degree of disorder, as obvious from their large thermal ellipsoids (Figure 1). C212 could not be modelled adequately with an anisotropic refinement and was therefore refined isotropically. It was not possible to apply a split model for the refinement of the methyl groups. The quality of the data set is restricted by the fact that [Li₂(tF-BDC)(DMF)₂] only contains light elements so that mainly weak high angle reflections are obtained. Reducing the 2θ range minimizes the *R* factors significantly, but a reflection:parameter ratio < 10 is obtained. Therefore, in the final refinement all measured reflections were used. Problems may also arise from the fact that a needle-shaped crystal was measured with a Stoe IPDS I diffractometer, which might lead to preferred orientation effects. A high standard deviation of the b axis (Table 1) is a hint for that. Nonetheless, the main conclusions of the crystal structure analysis are not influenced by these problems, so that no low temperature data were recorded. 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) with Ge monochromator and PSD detector. Samples were typically measured as flat samples for approx. 60 min with a step size 0.01° (2 θ). The WinXPow software package^[17] was used for data visu-

Table 1. Selected crystal and structure refinement data of $[Li_2(tF-BDC)(DMF_2]$ (Stoe IPDS I, Mo- K_a radiation, 20 °C).

Molecular formula, $M_{\rm r}$ /g·mol ⁻¹	C ₁₄ H ₁₄ F ₄ Li ₂ N ₂ O ₆ , 396.15
Crystal system, space group, Z	Orthorhombic, Pbcn, 8
a /Å, b /Å, c /Å	19.149(1), 9.714(4), 18.589(1)
$V/Å^3$	3458(1)
$D / \text{g·cm}^{-3}, \mu / \text{mm}^{-1}$	1.522, 0.14
Crystal size /mm ³	$0.3 \times 0.2 \times 0.1$
$\Theta_{\rm max}$ /°	26.8
Number of reflections	
measured	41904
independent	3689 [2105 with $I > 2\sigma(I)$]
Number of parameters	252
R factors	
$I_{\rm o} > 2\sigma(I_{\rm o})$	$R_1 = 0.088, wR_2 = 0.248$
All data	$R_1 = 0.129, wR_2 = 0.294$
R _{int} ; GooF	0.189; 1.02
$\Delta \rho_{\min/\max}$ /e·Å ⁻³	-0.63 / 1.18 ^{a)}

a) 1.74 Å from N310.

alization and calculation of theoretical XRD patterns from single crystal data.

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 Netzsch STA 409C/CD using an Al_2O_3 crucible in a constant argon stream (50 mL·min⁻¹). The heating rate was 10 °C·min⁻¹ with a sample mass of 20.4 mg.

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-978884 [Li₂(tF-BDC)(DMF)₂] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Additional experimental and simulated X-ray powder diffraction patterns, IR spectrum, DTA/TG plot and snapshot of the synthesis of [Li₂(tF-BDC)(DMF)₂].

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