Synthesis and Structural Characterization of Diisopropylammonium Trifluoroacetate and Diisoproplyammonium Pentafluoropropionate

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Diisopropylammonium trifluoroacetate ($\{[^i\mathrm{Pr}_2\mathrm{NH}_2][\mathrm{CF}_3\mathrm{COO}]\}$; dip tfa; **1**) and diisopropylammonium pentafluoropropionate ($\{[^i\mathrm{Pr}_2\mathrm{NH}_2][\mathrm{C}_2\mathrm{F}_5\mathrm{COO}]\}$; dip pfp; **2**) have been synthesized and structurally characterized by X-ray diffraction and spectroscopic methods. Both compounds form hydrogen-bonded cyclic dimers (Etter symbol: $R_4^4(12)$) in the solid state. The asymmetric unit of **1** contains one trifluoroacetate anion and one dip cation in the centrosymmetric space group $P\bar{1}$. The asymmetric unit of **2** consists of two crystallographically independent pentafluoropropionate anions and two independent dip cations forming dimers in the form of rings, both lying around centers of symmetry in the space group $P\bar{1}$. In dip tfa and dip pfp the cations act as double hydrogen bond donors, and each of the two oxygen atoms of the carboxyl group are single hydrogen bond acceptors. The donor acceptor distances of the N–H$\cdots$O hydrogen bonds are within the expected range for medium strong hydrogen bonds. The quasi-molecular cyclic dimers are connected with neighboring units only by van der Waals interactions.

Key words: Diisopropylammonium Cation, Hydrogen Bonding, Crystal Engineering, Carboxylates

Introduction

Synthesis and structural characterization of several diisopropylammonium (dip) salts gave a deeper insight into the dependency of the hydrogen bond characteristics of a series of selected anions as hydrogen bond acceptors. The structure types characterized so far are: a quasi-molecular unit in dip$_2$[SiF$_6$] [1], cyclic dimers with the Etter symbol $R_4^4(12)$ [2] for dip[Ph$_3$CO$_2$] [3], dip[ClO$_4$] [4], dip[(CH$_3$)$_2$CH]NCS$_2$] [5] and dip[*o*-MeO(C$_6$H$_4$)-CH-C(SH)(CO$_2$)Sn(C$_6$H$_5$)$_3$] [6], and catena (chain-type) structures for some halides and complex anions (dipCl [7, 8], dipCl $\cdot$ 0.5H$_2$O [9], dipCl $\cdot$ CHCl$_3$ [10], dipBr [11 – 13], dipI [11], dip[HF$_2$] [14], dip[ClO$_4$] [4], dip[NO$_3$] [15]). More complex systems with hydrogen bond-accepting subunits best described as dip dicarboxylates [16 – 18] also form one-dimensional hydrogen bonded chains. A two-dimensional network is found for dip$_2$[SO$_4$] [19], and a three-dimensional network with only weak hydrogen bonds in dip$_2$[IrCl$_6$] [20]. The analysis of the hydrogen bonding motifs found for the various salts may lead to the prediction of the structure types of newly synthesized dip salts. This prediction is based on the analysis of the hydrogen bond characteristics of the various anions in interplay with the dip cation and follows some principal rules.

The strength of the hydrogen bonds to the dip cation and the geometry and the net charge of the anions are important features that determine the formation of the principal structure type of the alkylammonium salts in the dip salt systems. Previous general investigations on the pure existence and the strength of classical and non-classical hydrogen bonds have allowed the classification of the hydrogen bonds [21]. Taking these informations into account, electrostatically supported N–H$^+\cdots$F$^-$ hydrogen bonds should be very strong, and N–H$^+\cdots$O$^-$ and N–H$^+\cdots$Hal$^-$ (Hal = Cl, Br, I) hydrogen bonds strong to medium strong, while hydrogen bonds to complex anions like [ClO$_4$]$^-$ and [IrCl$_6$]$^{2-}$, with only a small partial charge on every hydrogen bond-accepting center, should be much weaker. It is also quite clear that anions like [SO$_4$]$^{2-}$, [ClO$_4$]$^-$ and [IrCl$_6$]$^{2-}$ as multiple hydrogen bond acceptors show a tendency to form polymeric structures and networks. Especially anionic and neutral tetrahedral hydrogen bond acceptors have been discussed as tetrahedral synthons for crystal engineering [22]. In

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the dip salt system stronger hydrogen bonds are associated with smaller and lower-dimensional building units, medium strong hydrogen bonds with one-dimensional and dimeric ion pairs, and the weaker hydrogen bonds with motifs of higher dimensionallity.

Besides the pure hydrogen bond functionality, the van der Waals interactions of the alkyl groups play an important role in the process of growing dip salt crystals and must be taken into account for crystal engineering in this system. As rotation of both isopropyl groups of the dip cation about the C–N bonds is in general possible, the dip cation is a flexible to semi-flexible building unit [23]. In all structures determined so far there is a general tendency of the aliphatic groups to interlink with each other and to form hydrophobic regions within the crystal. Our approaches to classify known and to predict unknown structures based on the characteristics of anions and cations in terms of hydrogen bonding and van der Waals interaction have given a rough estimate of the structure type formed, but did not provide the possibility to describe all the details already found for structures of dip salts. Even in this simple system several modifications of one compound can appear. As examples for one-dimensional chains, dipCl [7, 8] and dipBr [11 – 13] each form at least a monoclinic and an orthorhombic modification at r. t., and dipBr a further low-temperature modification [12] as well as solvates that preserve the one-dimensional polymeric structure type [7, 11]. For all simple solvate-free chain-type structures a slightly different interlocking of the general building motifs (the ammonium group of dip cations and the halide anions forming chains according to the Etter symbol C(4)) produces isostructural polymorphs. By contrast, for the dip salts of the anions I^-, $[HF_2]^-$ and $[NO_3]^-$ only one chain-type modification was found. This is plausible, because these bulky anions seem to intensify the interlocking of neighboring chains. A further illustrative example of the complexity of this system is the non-isostructural relation of two modifications found for dip$[ClO_4]$. This compound undergoes a monotropic first order phase transition [24] from a cyclic dimer to a chain-type modification near r. t. [4]. Considering the weak hydrogen bonds in dip$[ClO_4]$, chain-type, dimeric and perhaps even higher-dimensional structures are generally possible.

The structural similarities of the $[NO_3]^-$, $[ClO_4]^-$ and carboxylate anions can be described by the generalized synthon: dip$[O_2XR_y]$ (X = C, Cl, N; y = 1,2, R = O, C). These synthons can be considered as ion pairs consisting of the dip cation and an anion with two hydrogen bonds-accepting centers approximately 2.2 Å apart. The fact that polymorphic dip$[ClO_4]$ forms a chain-type and a cyclic dimeric structure, dip$[NO_3]$ exists in a chain-type structure, and dip$[Ph_3CCO_2]$ in a cyclic dimeric structure, motivated us to investigate dip salts including the synthons mentioned above. Anions that fit the criteria of the synthon definition are the easily accessible carboxylates.

Table 1. Hydrogen bond lengths (Å) and angles (deg) for **1** and **2**.

1

D–H···A	D–H	H···A	D···A	angle
N1–H2 O1	0.928(14)	1.869(14)	2.794(2)	175(2)
N1–H1 $O2^{\#1}$	0.954(13)	1.857(14)	2.807(2)	173.5(18)

Symmetry code: $^{\#1}$ $1-x, 2-y, -z$.

2

D–H···A	D–H	H···A	D···A	angle
N1–H1···O1	0.904(18)	1.87(2)	2.767(4)	170(3)
N1–H2···$O2^{\#1}$	0.892(19)	1.90(2)	2.767(4)	163(3)
N2–H3···O3	0.910(18)	1.86(2)	2.760(4)	167(3)
N2–H4···$O4^{\#2}$	0.895(18)	1.92(2)	2.780(4)	160(3)

Symmetry code: $^{\#1}$ $1-x, 1-y, 1-z$; $^{\#2}$ $1-x, -y, -z$.

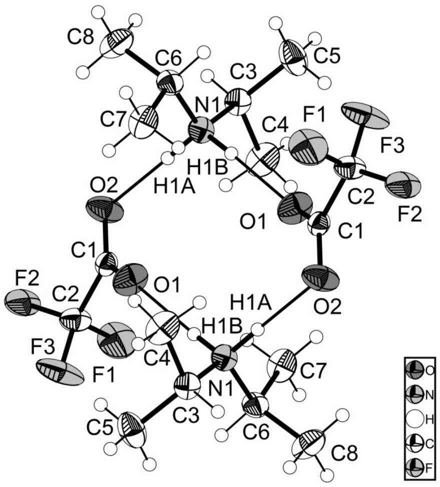

Fig. 1. The dimer of dip tfa (**1**) (displacement ellipsoids are drawn at the 40 % probability level, hydrogen atoms are drawn with arbitrary radii).

Results and Discussion

Fluorinated carboxylate anions are of interest for the synthesis of ionic liquids [25]. According to the terminology of crystal engineering, carboxylate anions combined with dip cations are potent synthons for the construction of one-dimensional chains or cyclic dimers. According to the terminology of Desiraju and

Table 2. Selected bond lengths (Å) and dihedral angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

1		**2**	
Distances			
C–C (cation)	1.512(3) – 1.521(3)	C–C (cations)	1.511(5) – 1.523(4)
C–C (anion)	1.537(4)	C–C (anions)	1.439(6) – 1.570(5)[a]
C–N	1.505(3); 1.509(3)	C–N	1.503(4) – 1.512(4)
C–F	1.299(3) – 1.346(3)[a]	C–F	1.339(5) – 1.427(7)[a]
C1–O1	1.237(2)	C1–O1	1.224(4)
C1–O2	1.235(3)	C1–O2	1.222(4)
		C10–O3	1.236(4)
		C10–O4	1.231(4)
Dihedral angles			
C6–N1–C3–C5	58.8(2)	C16–N2–C13–C15	58.1(4)
C6–N1–C3–C4	178.6(2)	C16–N2–C13–C14	178.8(3)
C3–N1–C6–C8	63.6(2)	C13–N2–C16–C17	59.1(4)
C3–N1–C6–C7	173.3(2)	C13–N2–C16–C18	177.5(3)
		C7–N1–C4–C5	59.48(4)
O2–C1–C2–F3	161.2(3)	C7–N1–C4–C6	177.1(3)
O1–C1–C2–F3	19.5(3)	C4–N1–C7–C9	60.5(4)
O2–C1–C2–F2	37.3(3)	C4–N1–C7–C8	176.9(3)
O1–C1–C2–F2	143.4(2)		
O2–C1–C2–F1	79.2(3)	O1–C1–C2–C3	105.8(5)
O1–C1–C2–F1	100.0(2)	O2–C1–C2–C3	74.9(6)
		O3–C10–C11–C12	28.8(5)
		O4–C10–C11–C12	155.8(4)

[a] A slight disorder of the CF_3 group in **1** and of the C_2F_5 groups in **2**, aggravated by pseudosymmetry effects, results in a high variance of the refined bond lengths of the C–F and C–C bonds in these groups.

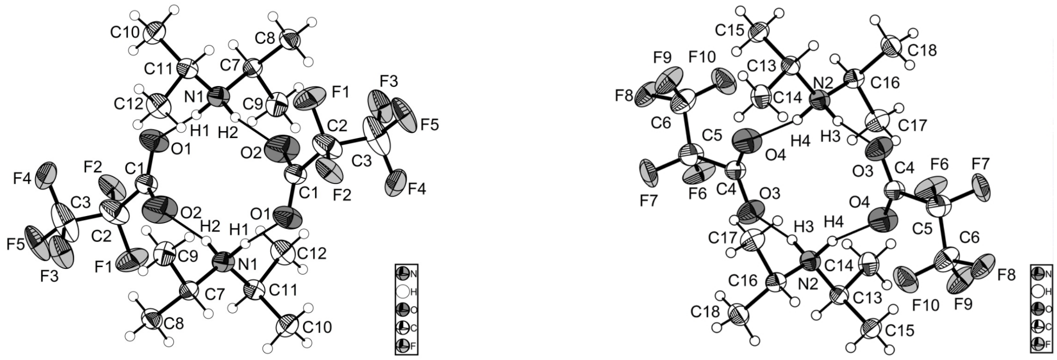

Fig. 2. Two crystallographically independent dimers of dip pfp (**2**) (displacement ellipsoids are drawn at the 50 % probability level, hydrogen atoms with arbitrary radii).

coworkers [26], the synthon $[RR'NH_2]^+[RCOO]^-$ can be classified as semi-robust, because there are two preferred structural motifs. Compounds **1** and **2** are easily accessible by reaction of diisopropylamine with an excess of the corresponding carboxylic acid. Crystals are obtained at r. t. by reducing the volume of the mother liquor by evaporation.

Thermal analysis

DTA measurements of dip tfa (**1**) in the temperature range 30 – 150 °C have shown that the compound begins to melt at 125 °C. In the measured temperature range there is no phase transition detectable. The DTA measurements (temperature range −140 °C to 140 °C) of dip pfp (**2**) have shown a melting point at 79 °C.

IR and Raman spectroscopy

The IR and Raman spectra of dip tfa (**1**) and dip pfp (**2**) show the typical bands arising from the internal modes of the diisopropylammonium cation, which are known *e. g.* from the corresponding dip chloride [25], and the typical bands of the perfluorinated anions.

Crystal structures

Diisopropylammonium trifluoroacetate (dip tfa, 1)

In the crystal structure of dip tfa (**1**) all N–C, C–C, C–O, and C–F bond lengths are in the expected range. There is one formula unit in the asymmetric unit in the centrosymmetric space group $P\bar{1}$. The structure

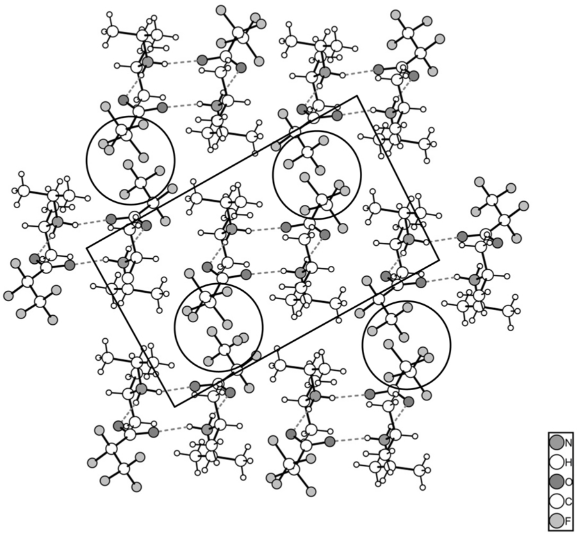

Fig. 3. Packing of the two crystallographically independent dimers of dip pfp (**2**) (circles highlight the interlocking of the pentafluoroethyl groups).

consists of centrosymmetric, hydrogen-bonded, cyclic dimers that are composed of two dip cations and two tfa anions arranged as rings (Fig. 1). The Etter symbol for these hydrogen bonded dimers is $R_4^4(12)$. The packing of the quasi-molecular dimeric units in the crystal structure results in hydrophobic regions formed by the aliphatic diisopropyl groups. The N–H···O hydrogen bonds with donor-acceptor distances close to 2.8 – 2.9 Å (Table 1) are in the class of medium strong hydrogen bonds.

*Diisopropylammonium pentafluorpropionate (dip pfp, **2**)*

In the crystal structure of dip pfp (**2**) the N–C, C–C, C–O and C–F bond lengths are all in the expected range (Table 2). In this structure two crystallographically independent, hydrogen-bonded, cyclic dimers are found both lying on different centers of symmetry in the space group $P\bar{1}$. The basic hydrogen bonding motif (Etter symbol: $R_4^4(12)$) is identical for both independent dimers in **2** and very similar to other dimeric species (for example in **1**, in dipPh$_3$CCO$_2$ [3], dipClO$_4$ [4] and dip[*o*-MeO(C$_6$H$_4$)-CH-C(SH)(CO$_2$)Sn(C$_6$H$_5$)$_3$] [6]). The existence of two crystallographically independent species in **2** (Figs. 2a and b) is obviously caused by the fact that the C$_2$F$_5$ groups – having different conformations – effectively interlink with neighboring C$_2$F$_5$ groups (Fig. 3). Although the salts **1** and **2** crystallize in dimers, it is possible that other structure types – *e. g.* catena (chain-type) structures – may be obtained for the dip/acetate synthon. Since according to literature, catena structures grow more quickly than lower-dimensional motifs [20, 21], quasi-molecular units or three-dimensional networks are less probable. Finally it is important to keep in mind a statement of Desiraju: “Given a collection of molecules that can come together in many ways, the favored route has little to do with the stability of the final ensemble, but rather with how fast this route can be travelled.” [26]. For the dip[O$_2XR_y$] (X = C, Cl, N; y = 1, 2, R = O, C) synthon it seems to be in fact a question of optimization of the system substituents R and conditions of crystallization (anion surplus in solution, the concentration of the salt, and the pH value, amongst others) to afford other structure types. As a consequence of our observation a general tendency for the dip[O$_2XR_y$] (X = C, Cl, N; y = 1, 2, R = O, C) synthon to form dimeric species can be noticed.

Conclusion

Two new structures with dip fluorocarboxylate synthons have been synthesized and structurally characterized. Common to both structures is the basic hydrogen bonding motif of a cyclic dimer with the Etter symbol $R_4^4(12)$. The quasi-molecular dimers are connected to neighboring units *via* van der Waals interactions only.

Experimental Section

The IR spectra were recorded on a single crystal with a Bio-Rad Excalibur FTS 3500 FT-IR spectrometer (Fa. Digilab former Bio-Rad GmbH, Germany) in the range of 4000 – 500 cm^{-1}. The single-crystalline samples were placed on a MIRacle single refraction ATR sample plate (ZnSe). A powder sample of the compounds was used to record the Raman spectra in the range 3400 – 70 cm^{-1} with the FT-IR Accessory (Bio-Rad GmbH, Germany) attached to the FT-IR spectrometer mentioned above. The thermogravimetric studies were performed using 5 – 10 mg powder samples in a Mettler DSC 30 instrument working with software version 8.10, 2004.

Synthesis

*Diisopropylammonium trifluoroacetate (**1**)*

At r. t., 7.1 mmol diisopropylamine is added to 21 mmol trifluoroacetic acid producing a colorless solution. From this solution, small thin platelets are obtained within a week. The crystals can be investigated under ambient conditions. – IR (single-crystal sample): ν (cm^{-1}) = 3047(m), 2988(m), 2946(m), 2880(m), 2847(m), 2784(m), 2784(m), 2739(m), 2583(w), 2501(w), 1782(vw), 1671(vs), 1599(w), 1493(w), 1466(w), 1427(m), 1398(m), 1317(vw), 1175(s), 1153(s), 1123(s), 956(vw), 838(w), 828(m), 799(m), 718(m). – Raman (powder sample): ν (cm^{-1}) = 2990(s), 2943(s), 2750(w), 1668(w), 1458(m), 1427(s), 1346(w), 1316(w), 1207(w), 1188(w), 1147(w), 1096(w), 954(w), 912(w), 833(m), 804(m), 717(w), 471(w), 433(w), 401(w).

*Diisopropylammonium pentafluoropropionate (**2**)*

3.5 mmol diisopropylamine is added to 10.6 mmol pentafluoropropionic acid at r. t. Within a few days a colorless solid forms in the solution. Concentration of the solution gives colorless crystals. – IR (single-crystal sample): ν (cm^{-1}) = 3053(m), 2991(m), 2949(m), 2877(m), 2783(m), 2741(m), 2582(w), 2498(w), 1770(vw), 1674(vs), 1586(w), 1489(w), 1471(w), 1398(m), 1321(vw), 1204(s), 1156(vs), 1102(w), 1025(s), 955(vw), 838(vw), 809(w), 776(vw), 727(m). – Raman (powder sample): ν (cm^{-1}) = 2993(s), 2951(s), 2750(w), 1664(w), 1458(m), 1432(m), 1404(m), 1344(w), 1313(w), 1183(w), 1146(w), 1097(w), 975(w), 911(w), 836(w), 814(m), 771(w), 726(w), 467(w), 386(w), 316(w).

*Diisopropylammonium chloride (**3**)*

IR (single-crystal sample): ν (cm^{-1}) = 3522(s), 3455(m), 3165(w), 2966(vs), 2911(s), 2836(vs), 2818(s), 2774(m), 2757(s), 2723(vs), 2646(w), 2536(w), 2480(s), 2418(w), 2084(w), 1582(w), 1476(m), 1465(m), 1457(m), 1439(m), 1395(m), 1378(m), 1354(w), 1328(w), 1305(w), 1202(w), 1182(w), 1152(m), 1100(m), 975(w), 957(w), 946(w), 915(w), 836(w), 803(w). – Raman (powder sample): ν (cm^{-1}) = 3456(w), 3164(w), 2988(vs), 2959(s), 2923(s), 2820(m), 2770(w), 2741(w), 2643(w), 2482(w), 2411(w), 1585(w), 1481(m), 1461(m), 1419(m), 1394(w), 1344(w), 1305(w), 1177(w), 1147(w), 1095(w), 970(w), 952(w), 915(w), 834(w), 802(m), 501(w), 470(m), 444(w), 376(w), 321(m), 197(w), 130(w).

Crystal structure determinations

Suitable single crystals were sealed in glass capillaries and examined on a Stoe one-circle IPDS diffractometer with MoK_α radiation (λ = 0.71073 Å).

$C_8O_2H_{16}NF_3$ *(1)*: M = 215.22 g mol^{-1}, crystal size = 0.5 × 0.2 × 0.5 mm^3, triclinic, space group $P\bar{1}$, a = 7.8751(13), b = 8.3843(13), c = 9.6509(15) Å, α = 74.860(18), β = 82.750(19), γ = 66.343(17)°, V = 563.2(15) Å^3, T = 293 K, Z = 2, $\rho_{\text{calcd.}}$ = 1.27 g cm^{-3}, μ(MoK_α) = 0.1, 7419 reflections measured (R_{int} = 0.0593), $2\theta_{\max}$ = 50°, *hkl* range: ±9, ±9, ±11, 1867 reflections unique, 2304 reflections observed [with $F^2 \geq 2\sigma(F^2)$], full-matrix least-squares refinement of 135 parameters on F^2, $wR2$ = 0.1063, $wR2$ (all data) = 0.1372, $R1$ = 0.0505, GooF = 1.003, $\Delta\rho_{\text{fin}}$ (max / min), 0.44 / −0.31 e Å^{-3}.

$C_{18}O_4H_{32}N_4F_{10}$ *(**2**)*: M = 558 g mol^{-1}, crystal size = 0.12 × 0.8 × 0.8 mm^3, triclinic, space group $P\bar{1}$, a = 8.9258(9), b = 9.9886(10), c = 15.3776(13) Å, α = 92.070(11), β = 102.676(10), γ = 107.949(11)°, V = 1264.5(2) Å^3, T = 293 K, Z = 2, $\rho_{\text{calcd.}}$ = 1.39 g cm^{-1}, μ(MoK_α) = 0.1, 16582 reflections measured (R_{int} = 0.0436), $2\theta_{\max}$ = 50°, *hkl* range: ±10, ±11, ±18, 4180 reflections unique, 2304 reflections observed [with $F^2 \geq 2\sigma(F^2)$], full-matrix least-squares refinement of 323 parameters on F^2, $wR2$ = 0.1013, $wR2$ (all data) = 0.1372, $R1$ = 0.0649, GooF = 1.001, $\Delta\rho_{\text{fin}}$ (max / min), 0.59 / −0.41 e Å^{-3}.

CCDC 725783 and 725784 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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