TU Clausthal

Crystal structure of $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

Introduction

Water immiscible ionic liquids are emerging as indispensable reagents for the solubilization of highly polar species, which display poor solubility properties in common solvents [1]. These solvents have been obtained in anhydrous form by an azeotropic distillation utilizing benzene, enabling work with compounds that hydrolyze in the presence of water. We here present a calcium species based on the reaction of CaH_2 with 1-n-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide.

Experimental

The ionic liquid was prepared by following the literature pathway and applying of inert gas techniques. After the treatment of $[(MeBuIm)_2][Ca(NTf_2)_4]$ with CaH_2 the compound was put under vacuum and stirred at 70°C. The reaction mixture was cooled down to -23°C and clear colorless blocks were obtained.

Characterization

The crystal structure crystallize in the monoclinic space group *P*2/*n* with two formula units in the unit cell (Fig. 1). Calcium is coordinated by ten oxygen atoms of four NTf_2 anions forming a slightly distorted square antiprism (Fig. 2) with Ca ─ O bond distances ranging from 2.348 to 2.487 Å. This metal environment is similar to the calcium environment in a similar compound [2]. Bond length and angle data for $[MeBuIm]^+$ cation in this salt, agree with previously reported imidazolium cations. The imidazole ring remains planar and the bond lengths in the imidazolium ring show strong residual double bond character at C(6) ─ C(7) with only partial delocalization of the positive charge, as previously reported [3]. The NTf_2 anion conformation in the title compound differs from that observed in the organic NTf_2 salt structures previously reported [4] and has the two S ─CF_3 groups oriented *cis* to one another. conformation. The anion as a whole has a near C_2 symmetry, and the sulfonyl moieties have distorted tetrahedral symmetry with bond angles ranging from 108 to 111 (Fig. 3).

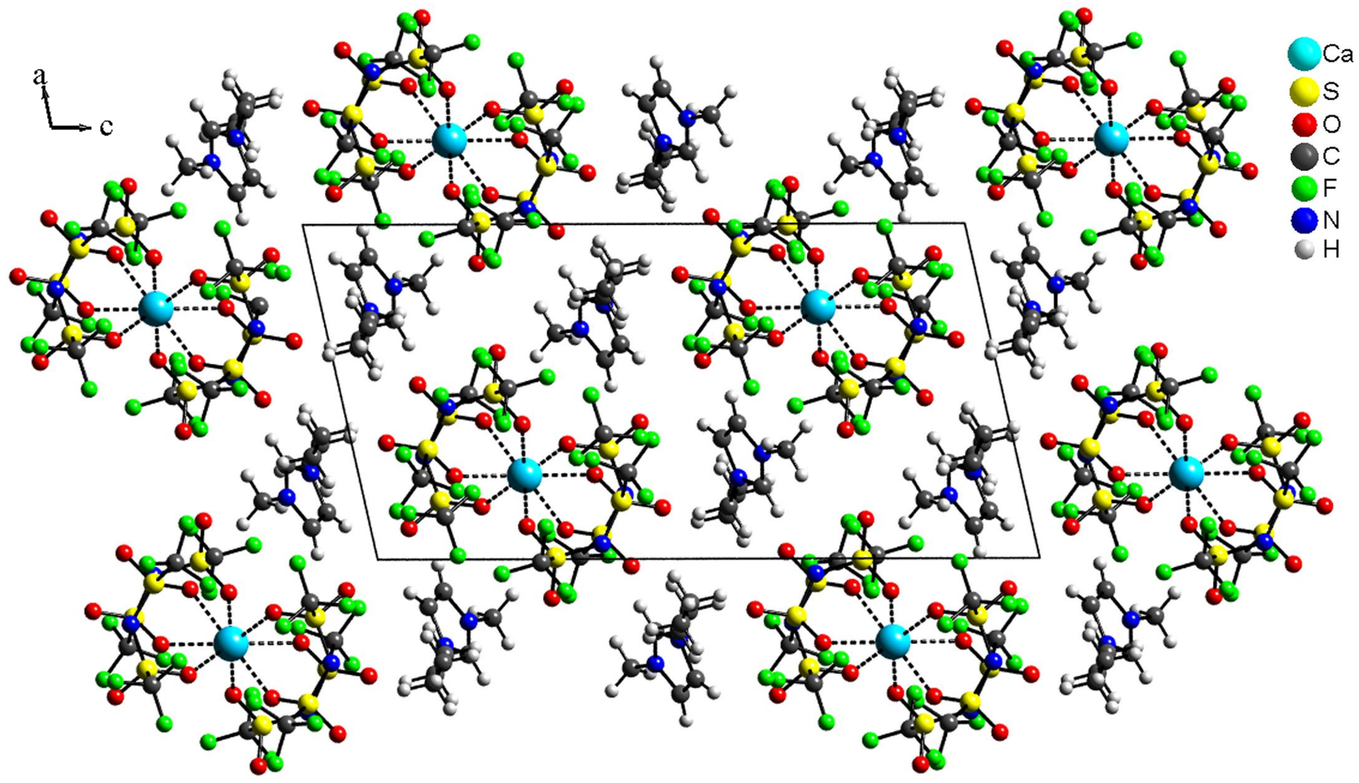

Fig. 1: Solid state structure of $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$ along *b* axis

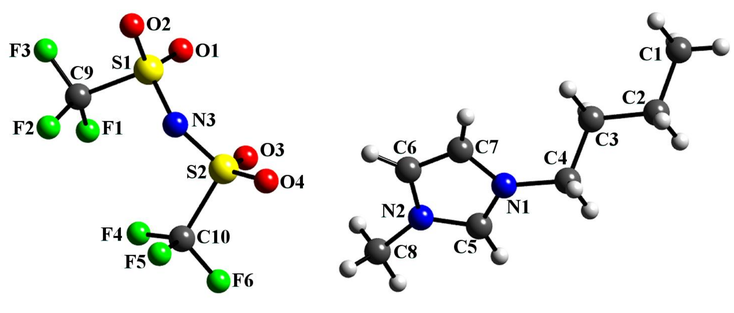

Fig. 3: $[(MeBuIm)]$ $[(NTf_2)]$

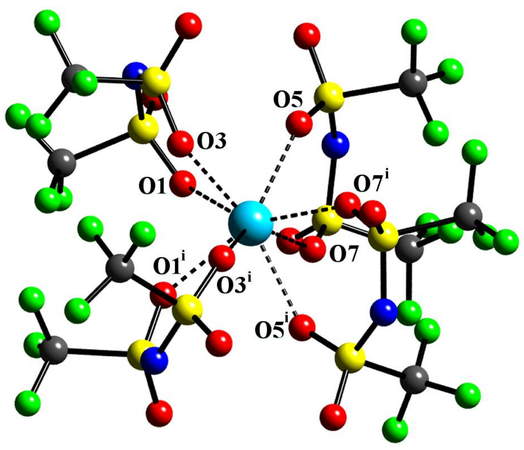

Fig. 2: Ca ─ coordination in $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

Table 1: Crystal data for $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

Empirical formula	$C_{24}H_{30}CaF_{24}N_8O_{16}S_8$
Formula weight	1439.12
Crystal system	monoclinic
Z	2
Space group	*P*2/*n* (Nr. 13)
a [Å]	11.0567(6)
b [Å]	11.3134(6)
c [Å]	21.3566(12)
β [ ]	102.50(1)
Volume [Å³]	2608.1(2)
Reflections collected	26972
R_{int}	0.0269
Data / restraints / parameters	6497 / 0 / 366
GooF	1.075
Final R indices [I>2σ(I)]	*R1* = 0.0359
	wR2 = 0.0863
R indices (all data)	*R1* = 0.0413
	wR2 = 0.0894

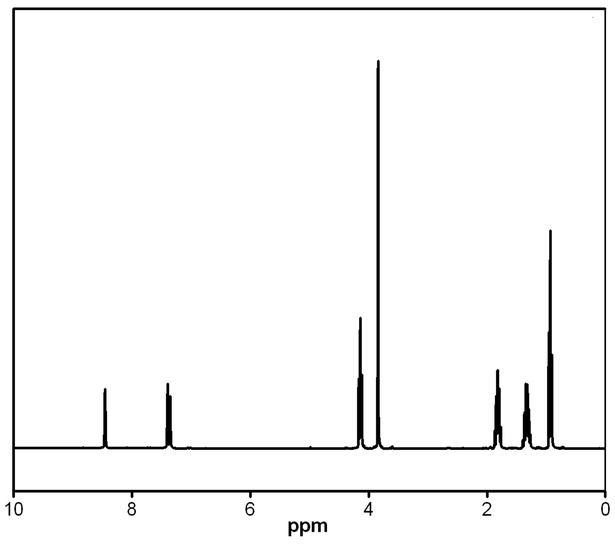

Fig. 4: ^1H ─ NMR of $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

Table 3: Atomic coordinates and equivalent isotropic displacement parameters in $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

	x / a	y / b	z / c	U_{eq} / Å²
Ca(1)	1/4	0.9073(1)	1/4	0.0135(1)
S(1)	0.1723(1)	0.2859(1)	0.1142(1)	0.0163(1)
O(1)	0.1572(1)	0.2388(1)	0.1749(1)	0.0182(1)
O(2)	0.926(1)	0.2411(1)	0.578(1)	0.0264(1)
C(1)	0.1278(2)	0.4419(2)	0.1163(1)	0.0243(1)
F(1)	0.107(1)	0.4478(1)	0.1223(1)	0.0342(1)
F(2)	0.1373(1)	0.4953(1)	0.6261(1)	0.040(1)
F(3)	0.1983(1)	0.4971(1)	0.1654(1)	0.032(1)
N(1)	0.3091(1)	0.2942(1)	0.1053(1)	0.019(1)
S(2)	0.4305(1)	0.2568(1)	0.1540(1)	0.016(1)
O(3)	0.4130(1)	0.1837(1)	0.2067(1)	0.018(1)
O(4)	0.5209(1)	0.2200(1)	0.1194(1)	0.024(1)
C(2)	0.4919(2)	0.3952(2)	0.1933(1)	0.022(1)
F(4)	0.4886(1)	0.4803(1)	0.1505(1)	0.032(1)
F(5)	0.4266(1)	0.4286(1)	0.2351(1)	0.030(1)
F(6)	0.6085(1)	0.3783(1)	0.2240(1)	0.038(1)
S(3)	0.3271(1)	-0.695(1)	0.1125(1)	0.017(1)
O(5)	0.2479(1)	-0.227(1)	0.1437(1)	0.019(1)
O(6)	0.3478(1)	-0.292(1)	0.528(1)	0.032(1)
C(3)	0.2422(2)	-0.209(2)	0.931(1)	0.026(1)

Table 2: Selected bond lengths [pm] and angles [°] for $[(MeBuIm)_2]$ $[Ca(NTf_2)_4]$

Ca(1) ─ O(7)^i	2.348(1)
Ca(1) ─ O(7)	2.348(1)
Ca(1) ─ O(1)^i	2.392(1)
Ca(1) ─ O(1)	2.392(1)
Ca(1) ─ O(3)	2.436(1)
Ca(1) ─ O(3)^i	2.436(1)
Ca(1) ─ O(5)	2.487(1)
Ca(1) ─ O(5)^i	2.487(1)

Symmetry transformations: i) ─*x*+1/2, *y*,─*z*+1/2

References

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