Electronic Supplementary Information on

Sila-polyethers as *innocent* crystallization reagents for heavy alkali metal compounds

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Experimental details

Crystallographic details

RbOTf

Empirical formula	$C_4F_{12}O_{12}Rb_4S_4$
Formula weight	938.16
Temperature/K	100.0
Crystal system	monoclinic
Space group	*Cm*
a/Å	19.2895(8)
b/Å	23.4587(9)
c/Å	5.0673(2)
α/°	90
β/°	100.992(2)
γ/°	90
Volume/Å^3	2250.92(16)
Z	4
ϱ_{calc}g/cm^3	2.768
μ/mm^{-1}	9.166
F(000)	1760.0

Crystal size/mm^3	0.151 × 0.083 × 0.063
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.302 to 50.668
Index ranges	-23 ≤ h ≤ 23, -28 ≤ k ≤ 25, -6 ≤ l ≤ 6
Reflections collected	33902
Independent reflections	4201 [R_{int} = 0.0680, R_{sigma} = 0.0352]
Data/restraints/parameters	4201/458/317
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.0644, wR_2 = 0.1122
Largest diff. peak/hole / e Å^{-3}	1.18/-2.24
Flack parameter	0.51(3)

Details of crystal structure refinement: The structure was refined as an inversion twin (BASF 0.50618). All CF_3 groups and most SO_3 groups showed significant disorder, either by rotation about the C-S bond of the triflate anion or tilting of the C-S bond. Disordered atoms were refined isotropically and a number of strict SADI, DFIX and ISOR restraints had to be used to stabilize the refinement. Occupancies of disordered groups were constrained to values yielding a chemically reasonably disorder model. One triflate anion is disordered about the mirror plane in such a way that the PART instruction cannot be used to generate a correct bonding pattern here, although the overall disorder model is reasonable here.

α-CsOTf (100 K)

Empirical formula	$CCsF_3O_3S$
Formula weight	281.98
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.4549(6)
b/Å	6.0582(4)
c/Å	18.339(2)
α/°	90
β/°	91.922(9)
γ/°	90
Volume/Å^3	605.71(10)
Z	4
ϱ_{calc}g/cm^3	3.092
μ/mm^{-1}	6.456
F(000)	512.0
Crystal size/mm^3	0.09 × 0.066 × 0.036
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.444 to 57.996
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 8$, $-24 \le l \le 24$
Reflections collected	22166
Independent reflections	1609 [R_{int} = 0.0676, R_{sigma} = 0.0224]
Data/restraints/parameters	1609/0/82
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0207, wR_2 = 0.0502
Final R indexes [all data]	R_1 = 0.0239, wR_2 = 0.0511
Largest diff. peak/hole / e Å^{-3}	1.28/-0.86

α-CsOTf (293 K)

Empirical formula	$CCsF_3O_3S$
Formula weight	281.98
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.4705(11)
b/Å	6.1497(8)
c/Å	18.759(4)
α/°	90
β/°	91.357(16)
γ/°	90
Volume/Å^3	630.9(2)
Z	4
ϱ_{calc}g/cm^3	2.969
μ/mm^{-1}	6.198
F(000)	512.0
Crystal size/mm^3	0.09 × 0.066 × 0.036
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.344 to 57.992
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 8$, $-25 \le l \le 25$
Reflections collected	14785
Independent reflections	1680 [R_{int} = 0.0729, R_{sigma} = 0.0310]
Data/restraints/parameters	1680/0/82
Goodness-of-fit on F^2	0.979
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0579, wR_2 = 0.1048
Largest diff. peak/hole / e Å^{-3}	1.53/-0.73

$Cs_2C_2O_4$ (100 K)

Empirical formula	$C_2Cs_2O_4$
Formula weight	353.84
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.5506(4)
b/Å	10.8879(6)
c/Å	8.5685(6)
α/°	90
β/°	97.405(2)
γ/°	90
Volume/Å3	606.03(7)
Z	4
ϱcalcg/cm3	3.878
μ/mm-1	11.955
F(000)	616.0
Crystal size/mm3	0.117 × 0.081 × 0.066
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.082 to 50.54
Index ranges	-7 ≤ h ≤ 7, -13 ≤ k ≤ 13, -10 ≤ l ≤ 10
Reflections collected	6053
Independent reflections	1095 [Rint = 0.0329, Rsigma = 0.0217]
Data/restraints/parameters	1095/0/73
Goodness-of-fit on F2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0149, wR_2 = 0.0282
Final R indexes [all data]	R_1 = 0.0199, wR_2 = 0.0293
Largest diff. peak/hole / e Å-3	0.55/-0.58

Comparison of α-CsOTf (100 K), α-CsOTf (293 K) and α-CsOTf (Jansen)

Table S1: Comparison of unit cell parameters of single crystal measurements of α-CsOTf at 100 K and 293 K with data from previous work by *Jansen*.[1]

	α-CsOTf	**α-CsOTf**	**α-CsOTf (from powder data)[1]**
Temperature/K	100	293	294
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1$
a/Å	5.4549(6)	5.4705(11)	9.7406(2)
b/Å	6.0582(4)	6.1497(8)	6.1640(1)
c/Å	18.339(2)	18.759(4)	5.4798(1)
β/°	91.922(9)	91.357(16)	104.998(1)
Volume/Å^3	605.71(10)	630.9(2)	317.81(10)
Z	4	4	2

Table S2: Comparison of interatomic distances obtained from single crystal measurements of α-CsOTf at 100 K and 293 K with data from previous work by *Jansen*[1].

Interatomic distances in Å	**α-CsOTf (100 K, this work)**	**α-CsOTf (293 K, this work)**	**α-CsOTf (from powder data)**
S-C	1.819(3)	1.776(8)	1.805(7)
S-O	1.436(2)-1.438(2)	1.383(6) - 1.468(5)	1.432(10) - 1.444(13)
C-F	1.322(3)-1.328(3)	1.253(11) - 1.377(9)	1.311(11) - 1.320(15)
Cs-O	3.010(1)-3.361(1)	3.057(5) - 3.409(4)	2.969(12) - 3.330(16)
Cs-F	3.287(1)-3.653(2)	3.381(6) - 3.657(7)	3.492(12)- 3.847(11)

References

[1] L. Hildebrandt, R. Dinnebier and M. Jansen, *Z. Anorg. Allg. Chem.*, 2005, **631**, 1660–1666.