Crystal structure of potassium trifluoro[1,3-dithiano]borate, $K(C_4S_2H_7BF_3)$

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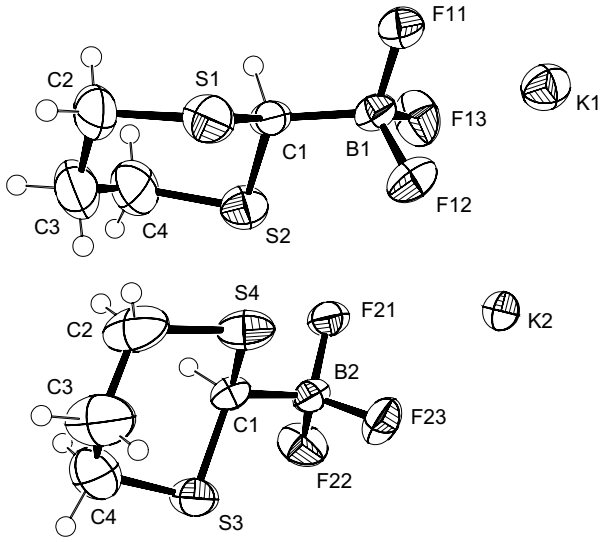

Abstract

$C_4H_7BF_3KS_2$, monoclinic, $P12_1/c1$ (no. 14), a = 14.7374(3) Å, b = 9.0612(1) Å, c = 13.5805(2) Å, β = 98.964(4)°, V = 1791.4 Å^3, Z = 8, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.010, T = 296 K.

Source of material

A solution of 1,3-dithiane (1,20 g, 10 mmol, 1 eq.) in 20 mL of dry THF was cooled to –78 °C under nitrogen. *n*-BuLi (6.66 mL, 1.5 M in hexane, 10 mmol, 1 eq.) was added dropwise, and the solution was stirred for 1 h at this temperature. Trimethylborate 1.34 mL (1.25 g, 12 mmol, 1.2 equiv.) was then added dropwise at –30 °C. The solution was stirred at this temperature for 1 h and one more hour at room temperature after which a saturated aqueous solution of potassium hydrogen difluoride (3.12 g, 40 mmol, 4.0 eq.) was added to the vigorously stirred solution. The resulting mixture was allowed to stir for 1 h at this temperature. Then the solvent was removed under reduced pressure, and the resulting white solid was dried under high vacuum for 2 h to remove all water. The solid was then washed with acetone and with hot acetone. The resulting organic solution was filtered, and the solvent was removed to afford a fluffy white solid. This solid was then dissolved in hot acetone and precipitated with diethyl ether, after which the solution was cooled to –20 °C to complete precipitation. The product was collected as a white crystalline solid (1.02 g, yield 63 %).

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Discussion

The title compound crystallizes as discrete K^+ and $C_4H_7BF_3S_2^-$ moieties, of which there are two independent formula units in the asymmetric unit. In the structure the K1 atom is surrounded by four anions making close contacts with seven F atoms with distances ranging from 2.639(1) Å to 2.970(1) Å. The K2 is surrounded by three anions making close contacts with five F atoms with distances ranging from 2.684(1) Å to 2.910 Å. The two 1,3-dithiano six-membered rings are in an almost undistorted chair conformation, the Cremer and Pople's ring-puckering parameters [1] being q_2 = 0.088(3) Å (0.065(2) Å), q_3 = 0.718(3) Å (0.695(2) Å), φ_2 = 7(2)° (–32(2)°), θ_2 = 7.0(3)° (5.3(2)°) and Q = 0.7233(2) Å (0.698(2) Å); the values in parentheses correspond to the ring attached to B2.

Table 1. Data collection and handling.

Crystal:	colorless irregular plate, size 0.03 × 0.10 × 0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.39 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, ω/φ, κ offsets
$2\theta_{max}$:	56.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18651, 4460
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3335
$N(param)_{refined}$:	199
Programs:	SIR92 [2], SHELXL-97 [3], PARST95 [4], PLATON [5], WinGX [6], ORTEP-3 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.2732	0.4573	0.2538	0.046
H(2A)	4*e*	0.4449	0.2617	0.1286	0.099
H(2B)	4*e*	0.4053	0.4165	0.1509	0.099
H(3A)	4*e*	0.4963	0.2295	0.3019	0.114
H(3B)	4*e*	0.5445	0.3631	0.2582	0.114
H(4A)	4*e*	0.4427	0.5239	0.3204	0.098
H(4B)	4*e*	0.5056	0.4383	0.4050	0.098
H(5)	4*e*	0.1875	0.8680	–0.0067	0.045
H(6A)	4*e*	0.2468	0.6244	–0.2208	0.068
H(6B)	4*e*	0.2689	0.7777	–0.1694	0.068
H(7A)	4*e*	0.3152	0.5056	–0.0737	0.071
H(7B)	4*e*	0.3857	0.6046	–0.1188	0.071
H(8A)	4*e*	0.3640	0.7914	–0.0033	0.072
H(8B)	4*e*	0.4088	0.6486	0.0479	0.072

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	4*e*	–0.00044(3)	0.07436(5)	0.21658(3)	0.0484(2)	0.0387(2)	0.0447(3)	–0.0025(2)	0.0063(2)	0.0019(2)
K(2)	4*e*	0.13741(3)	0.36456(5)	0.02374(3)	0.0569(3)	0.0531(3)	0.0326(2)	–0.0018(2)	0.0105(2)	0.0057(2)
S(1)	4*e*	0.31022(4)	0.23242(7)	0.19392(4)	0.0624(3)	0.0719(4)	0.0390(3)	0.0192(3)	0.0112(2)	–0.0036(3)
S(2)	4*e*	0.35592(4)	0.36504(7)	0.39834(4)	0.0569(3)	0.0690(4)	0.0392(3)	0.0012(3)	0.0015(2)	–0.0002(3)
S(3)	4*e*	0.14442(3)	0.67262(6)	–0.11309(3)	0.0510(3)	0.0442(3)	0.0264(2)	0.0006(2)	0.0051(2)	–0.0039(2)
S(4)	4*e*	0.26327(4)	0.67899(7)	0.08722(4)	0.0581(3)	0.0628(4)	0.0286(3)	0.0082(2)	0.0008(2)	0.0031(2)
B(1)	4*e*	0.1733(1)	0.3195(2)	0.3037(2)	0.047(1)	0.039(1)	0.032(1)	0.0009(9)	0.0096(9)	0.0043(9)
B(2)	4*e*	0.0774(2)	0.7703(3)	0.0554(2)	0.060(1)	0.042(1)	0.032(1)	0.010(1)	0.011(1)	–0.002(1)
F(11)	4*e*	0.10767(8)	0.3421(1)	0.21604(9)	0.0471(6)	0.0641(8)	0.0368(6)	–0.0019(5)	0.0038(5)	0.0082(6)
F(12)	4*e*	0.16300(9)	0.1729(1)	0.3318(1)	0.0667(8)	0.0478(7)	0.0638(8)	–0.0056(6)	0.0163(6)	0.0196(6)
F(13)	4*e*	0.14635(8)	0.4078(2)	0.3781(1)	0.0554(7)	0.080(1)	0.0526(8)	0.0047(6)	0.0164(6)	–0.0224(7)
F(21)	4*e*	0.0868(1)	0.8586(2)	0.1402(1)	0.0801(9)	0.095(1)	0.0427(7)	0.0281(8)	0.0051(7)	–0.0283(7)
F(22)	4*e*	0.04992(9)	0.6275(2)	0.0826(1)	0.0751(8)	0.0563(8)	0.0650(9)	0.0127(6)	0.0351(7)	0.0210(7)
F(23)	4*e*	0.00359(8)	0.8251(1)	–0.01402(9)	0.0535(6)	0.0535(8)	0.0468(7)	0.0066(5)	0.0040(5)	0.0047(6)
C(1)	4*e*	0.2754(1)	0.3585(2)	0.2833(1)	0.0440(9)	0.038(1)	0.034(1)	0.0048(8)	0.0064(7)	0.0072(8)
C(2)	4*e*	0.4176(2)	0.3179(4)	0.1773(2)	0.052(1)	0.146(3)	0.053(2)	0.021(2)	0.020(1)	0.017(2)
C(3)	4*e*	0.4863(2)	0.3276(5)	0.2738(2)	0.048(1)	0.172(4)	0.067(2)	0.022(2)	0.013(1)	0.013(2)
C(4)	4*e*	0.4555(2)	0.4273(4)	0.3500(2)	0.046(1)	0.117(3)	0.079(2)	–0.009(1)	–0.002(1)	0.007(2)
C(5)	4*e*	0.1697(1)	0.7662(2)	0.0055(1)	0.055(1)	0.0314(9)	0.0259(9)	0.0016(8)	0.0019(8)	–0.0009(7)
C(6)	4*e*	0.2532(2)	0.6760(3)	–0.1575(2)	0.065(1)	0.074(2)	0.035(1)	–0.007(1)	0.018(1)	0.003(1)
C(7)	4*e*	0.3312(1)	0.6067(3)	–0.0869(2)	0.049(1)	0.081(2)	0.051(1)	–0.004(1)	0.021(1)	–0.002(1)
C(8)	4*e*	0.3527(2)	0.6886(3)	0.0106(2)	0.048(1)	0.075(2)	0.056(1)	–0.010(1)	0.003(1)	0.003(1)

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