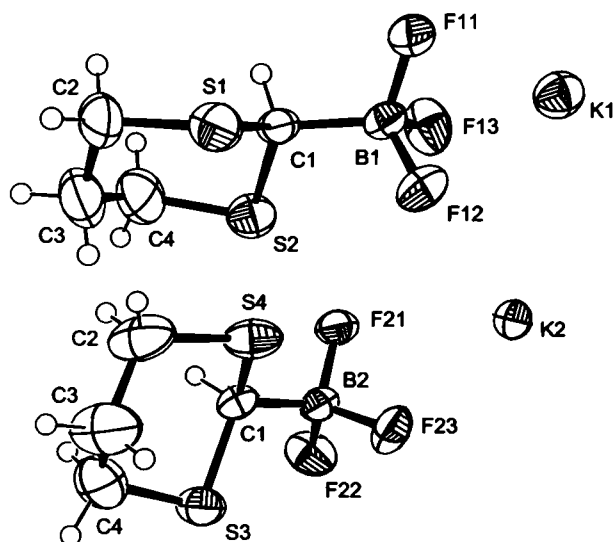


Crystal structure of potassium trifluoro[1,3-dithiano]borate, $K(C_4S_2H_7BF_3)$

H. A. Stefani^{*I}, R. Cella^{II}, J. Zukerman-Schpector^{III} and I. Caracelli^{*IV}^I Universidade de São Paulo, Faculdade de Ciências Farmacêuticas, Departamento de Farmácia, C.P. 26077, 05508-900 São Paulo, SP, Brazil^{II} Universidade de São Paulo, Instituto de Química, C.P. 26077, 05508-900 São Paulo, SP, Brazil^{III} Universidade Federal de São Carlos, Departamento de Química, Laboratório de Cristalografia, Estereodinâmica e Modelagem Molecular, C.P. 676, 13565-905 São Carlos, SP, Brazil^{IV} Universidade Estadual Paulista - UNESP/Bauru, Faculdade de Ciências, Departamento de Física, Av. Luiz Edmundo Carrijo Coube, 14-01, 17033-360 Bauru, SP, Brazil

Received April 4, 2006, accepted and available on-line April 24, 2006; CCDC no. 1267/1758



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, $\beta = 98.964(4)^\circ$, $V = 1791.4$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.029$, $wR_{\text{ref}}(F^2) = 0.010$, $T = 296$ 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 %).

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), $\varphi_2 = 7(2)^\circ$ ($-32(2)^\circ$), $\theta_2 = 7.0(3)^\circ$ ($5.3(2)^\circ$) 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 $0.03 \times 0.10 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	10.39 cm^{-1}
Diffractionmeter, scan mode:	Nonius KappaCCD, ω/φ , κ offsets
$2\theta_{\text{max}}$:	56.74°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	18651, 4460
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3335
$N(\text{param})_{\text{refined}}$:	199
Programs:	SIR92 [2], SHELXL-97 [3], PARST95 [4], PLATON [5], WinGX [6], ORTEP-3 [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

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

* Correspondence authors (e-mail: hstefani@usp.br, ignez@fc.unesp.br)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
K(1)	4e	−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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)	4e	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)

Acknowledgments. The authors gratefully acknowledge the financial support of, CNPq (JZ-S), FAPESP (05/59141-6 to HAS) and CAPES. We would like to thank Prof. Ernesto Shulz Lang of the Universidade Federal de Santa Maria, for the data collection.

References

- Cremer, D.; Pople, J. A.: General definition of ring puckering coordinates. *J. Am. Chem. Soc.* **97** (1975) 1354–1358.
- Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32** (1999) 115–119.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1990.
- Nardelli, M.: PARST95 – an update to PARST, a system of Fortran routines for calculating molecular structure parameters from the results of crystal structure analyses. *J. Appl. Crystallogr.* **28** (1995) 659.
- Spek, A. L.: Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **36** (2003) 7–13.
- Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32** (1999) 837–838.
- Farrugia, L. J.: ORTEP-3 for Windows – a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **30** (1997) 565.