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Tetraacetonitrilelithium tetraisothiocyanatoborate

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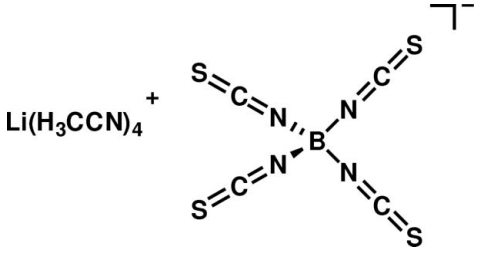
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.092; data-to-parameter ratio = 16.0.

The crystal structure of the title salt, $[Li(CH_3CN)_4][B(NCS)_4]$, is composed of discrete cations and anions. Both the Li and B atoms show a tetrahedral coordination by four equal ligands. The acetonitrile and isothiocyanate ligands are linear. The bond angles at the B atom are close to the ideal tetrahedral value [108.92 (18)–109.94 (16)°], but the bond angles at the Li atom show larger deviations [106.15 (17)–113.70 (17)°].

Related literature

Our group is interested in the synthesis of novel and improved electrolytes, namely borates with alkinyl or catecholate ligands, see: Lerner *et al.* (2007, 2012); Röder *et al.* (2008). For the preparation, see: Kleemann & Newman (1981).



Experimental

Crystal data

$[Li(C_2H_3N)_4](C_4BN_4S_4)$
M_r = 414.29
Monoclinic, $C2/c$
a = 21.219 (3) Å
b = 9.4756 (14) Å
c = 21.596 (4) Å
β = 92.845 (10)°
V = 4336.8 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 173 K
0.35 × 0.29 × 0.15 mm

Data collection

Stoe IPDS II two-circle diffractometer
Absorption correction: multi-scan (*X-AREA*; Stoe & Cie, 2001)
T_{min} = 0.858, T_{max} = 0.936
24466 measured reflections
3816 independent reflections
2681 reflections with $I > 2\sigma(I)$
R_{int} = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 0.97
3816 reflections
239 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5320).

References

Kleemann, L. P. & Newman, G. H. (1981). US Patent No. 4 279 976.
Lerner, H.-W., Röder, J., Vitze, H., Bolte, M., Wagner, M. & Wietelmann, U. (2007). Ger. Patent No. 10 2007 047 812 A1.
Lerner, H.-W., Röder, J., Vitze, H., Bolte, M., Wagner, M. & Wietelmann, U. (2012). US Patent No. 8 222 457.
Röder, J., Wietelmann, U., Vitze, H., Bolte, M., Lerner, H.-W. & Wagner, M. (2008). Ger. Patent No. 10 2008 041 812 A1.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2013). E**69**, m253 [https://doi.org/10.1107/S1600536813009082]

Tetraacetonitrilelithium tetraisothiocyanatoborate

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S1. Comment

Our group is interested in the synthesis of novel and improved electrolytes, namely, borates with alkinyl or catecholate ligands (Lerner *et al.*, 2007, 2012; Röder *et al.*, 2008). In the course of our investigations we synthesized the literature-reported borate $Li[B(NCS)_4]$ (Kleemann & Newman 1981) to compare its electrochemical properties with those of the borates which we have prepared. We were able to get crystals of this so far structurally uncharacterized borate $Li(CH_3CN)_4[B(NCS)_4]$. The borate $Li(CH_3CN)_4[B(NCS)_4]$ was synthesized from $BF_3(OEt_2)$ and Li[NCS], as shown in Figure 1.

The crystal structure of $[Li(CH_3CN)_4]^+[B(NCS)_4]^-$ is composed of discrete cations and anions (Fig. 2). Both the Li and B centre, show a tetrahedral coordination by four equal ligands. The acetonitrile and the isothiocyanate ligands are linear. Whereas the bond angles at the boron centre [108.92 (18)° - 109.94 (16)°] are very close to the ideal tetrahedral value, the bond angles around the Li centre [106.15 (17)° - 113.70 (17)°] show larger deviations from the ideal value.

S2. Experimental

$Li(CH_3CN)_4[B(NCS)_4]$: The borate $Li(CH_3CN)_4[B(NCS)_4]$ was prepared according to a literature procedure (Kleemann & Newman 1981). X-ray quality crystals of $Li(CH_3CN)_4[B(NCS)_4]$ were grown from an acetonitrile solution at room temperature.

S3. Refinement

All H atoms were located in difference Fourier maps. Nevertheless, they were geometrically positioned and refined using a riding model with C—H = 0.98 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$. The methyl groups were allowed to rotate but not to tip.

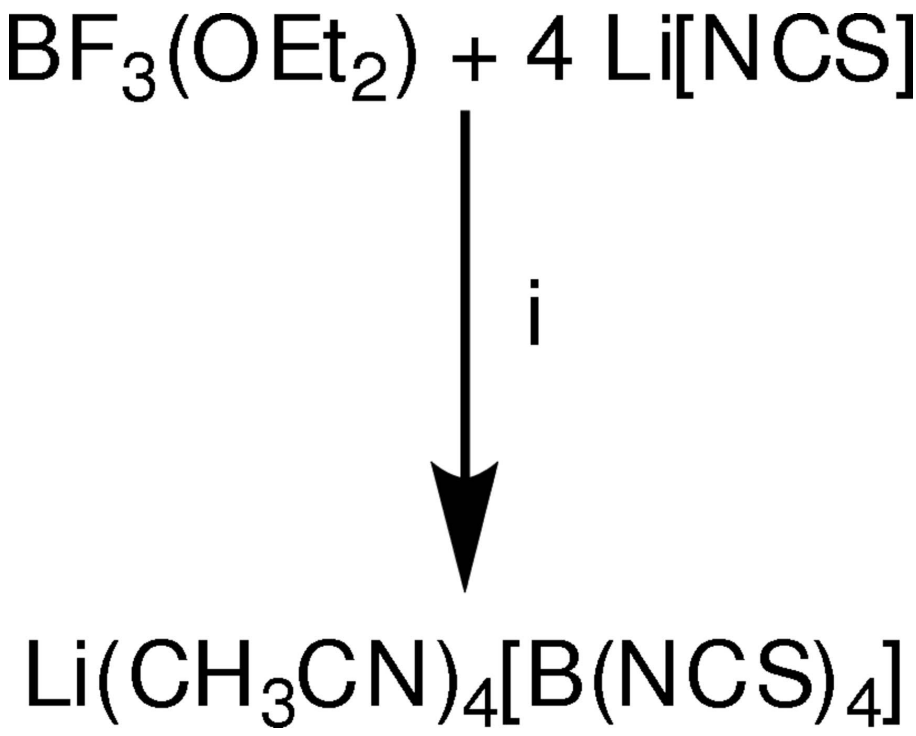

Figure 1

Synthesis of $Li(CH_3CN)_4[B(NCS)_4]$. (i) -3LiF; in CH_3CN.

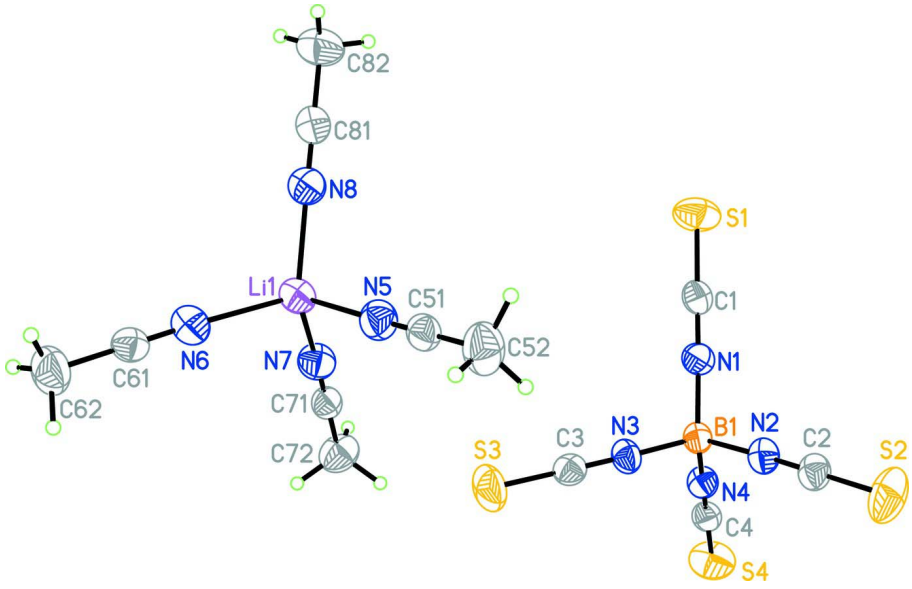

Figure 2

A perspective view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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Crystal data

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Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 21.219$ (3) Å
$b = 9.4756$ (14) Å
$c = 21.596$ (4) Å
$\beta = 92.845$ (10)°
$V = 4336.8$ (12) Å^3
$Z = 8$
$F(000) = 1696$
$D_x = 1.269$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 13942 reflections
$\theta = 3.6$–$26.8°$
$\mu = 0.45$ mm^{-1}
$T = 173$ K
Block, colourless
0.35 × 0.29 × 0.15 mm

Data collection

Stoe IPDS II two-circle diffractometer
Radiation source: Genix 3D IμS microfocus X-ray source
Genix 3D multilayer optics monochromator
ω scans
Absorption correction: multi-scan (*X-AREA*; Stoe & Cie, 2001)
$T_{min} = 0.858$, $T_{max} = 0.936$
24466 measured reflections
3816 independent reflections
2681 reflections with $I > 2\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.6°$
$h = -25 \rightarrow 25$
$k = -11 \rightarrow 11$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 0.97$
3816 reflections
239 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.032$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
B1	0.60133 (11)	0.2457 (2)	0.70356 (11)	0.0313 (4)
N1	0.61748 (7)	0.15384 (18)	0.65017 (8)	0.0385 (4)
C1	0.62999 (8)	0.0914 (2)	0.60595 (10)	0.0353 (4)

S1	0.64743 (3)	0.00457 (7)	0.54619 (3)	0.06209 (19)
N2	0.65695 (7)	0.33656 (17)	0.72237 (8)	0.0378 (4)
C2	0.69788 (9)	0.4127 (2)	0.73635 (9)	0.0384 (5)
S2	0.75423 (3)	0.51599 (7)	0.75594 (3)	0.0673 (2)
N3	0.54597 (7)	0.33778 (16)	0.68497 (7)	0.0355 (4)
C3	0.50357 (8)	0.4078 (2)	0.66964 (8)	0.0346 (4)
S3	0.44491 (3)	0.50352 (7)	0.64826 (3)	0.06058 (19)
N4	0.58433 (7)	0.15490 (16)	0.75811 (8)	0.0355 (4)
C4	0.57138 (8)	0.0892 (2)	0.80105 (9)	0.0349 (4)
S4	0.55383 (3)	−0.00256 (7)	0.85961 (3)	0.06261 (19)
Li1	0.34824 (15)	0.4840 (3)	0.44482 (16)	0.0416 (8)
N5	0.42234 (8)	0.6002 (2)	0.47394 (8)	0.0461 (4)
C51	0.46315 (9)	0.6718 (2)	0.48727 (9)	0.0389 (5)
C52	0.51502 (11)	0.7646 (3)	0.50381 (13)	0.0613 (7)
H52A	0.5480	0.7536	0.4740	0.092*
H52B	0.5323	0.7409	0.5455	0.092*
H52C	0.5001	0.8625	0.5033	0.092*
N6	0.27497 (8)	0.61203 (19)	0.42481 (8)	0.0464 (4)
C61	0.23575 (9)	0.6908 (2)	0.41537 (9)	0.0386 (5)
C62	0.18563 (11)	0.7913 (3)	0.40324 (13)	0.0620 (7)
H62A	0.1819	0.8524	0.4395	0.093*
H62B	0.1458	0.7410	0.3948	0.093*
H62C	0.1952	0.8490	0.3672	0.093*
N7	0.32273 (8)	0.36138 (19)	0.51545 (9)	0.0461 (4)
C71	0.30814 (8)	0.3053 (2)	0.55915 (10)	0.0364 (4)
C72	0.28959 (12)	0.2348 (3)	0.61477 (11)	0.0542 (6)
H72A	0.3192	0.2594	0.6494	0.081*
H72B	0.2901	0.1324	0.6083	0.081*
H72C	0.2469	0.2647	0.6243	0.081*
N8	0.37312 (8)	0.36597 (19)	0.37288 (9)	0.0444 (4)
C81	0.38851 (9)	0.3023 (2)	0.33200 (11)	0.0398 (5)
C82	0.40806 (13)	0.2207 (3)	0.27914 (13)	0.0646 (7)
H82A	0.3716	0.1704	0.2603	0.097*
H82B	0.4405	0.1525	0.2930	0.097*
H82C	0.4253	0.2844	0.2485	0.097*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.0281 (9)	0.0337 (10)	0.0321 (11)	0.0005 (8)	0.0013 (8)	0.0031 (9)
N1	0.0373 (8)	0.0408 (9)	0.0376 (10)	0.0027 (7)	0.0043 (7)	−0.0003 (8)
C1	0.0313 (9)	0.0317 (10)	0.0429 (12)	−0.0012 (7)	0.0029 (8)	0.0024 (9)
S1	0.0764 (4)	0.0521 (4)	0.0592 (4)	−0.0026 (3)	0.0184 (3)	−0.0211 (3)
N2	0.0326 (8)	0.0397 (9)	0.0408 (10)	−0.0015 (7)	0.0002 (7)	0.0026 (7)
C2	0.0355 (10)	0.0433 (11)	0.0362 (11)	0.0007 (9)	−0.0006 (8)	0.0079 (9)
S2	0.0574 (4)	0.0733 (4)	0.0692 (4)	−0.0323 (3)	−0.0161 (3)	0.0098 (3)
N3	0.0304 (8)	0.0381 (9)	0.0379 (9)	0.0059 (7)	0.0014 (7)	0.0063 (7)
C3	0.0363 (10)	0.0379 (10)	0.0299 (10)	−0.0035 (8)	0.0042 (8)	0.0033 (8)

S3	0.0462 (3)	0.0712 (4)	0.0640 (4)	0.0258 (3)	−0.0017 (3)	0.0165 (3)
N4	0.0356 (8)	0.0364 (8)	0.0345 (9)	0.0019 (7)	0.0018 (7)	0.0053 (8)
C4	0.0346 (9)	0.0342 (10)	0.0358 (11)	0.0057 (8)	0.0012 (8)	−0.0002 (9)
S4	0.0843 (4)	0.0581 (4)	0.0470 (4)	0.0039 (3)	0.0194 (3)	0.0217 (3)
Li1	0.0411 (16)	0.0402 (18)	0.0440 (19)	0.0036 (15)	0.0058 (14)	−0.0016 (16)
N5	0.0415 (9)	0.0511 (11)	0.0457 (11)	−0.0003 (8)	0.0024 (8)	0.0040 (8)
C51	0.0370 (10)	0.0427 (11)	0.0369 (11)	0.0075 (9)	0.0026 (8)	0.0065 (9)
C52	0.0456 (14)	0.0583 (15)	0.0791 (19)	−0.0065 (10)	−0.0060 (13)	−0.0049 (13)
N6	0.0430 (9)	0.0462 (10)	0.0503 (11)	0.0022 (8)	0.0063 (8)	0.0010 (8)
C61	0.0400 (10)	0.0378 (11)	0.0382 (11)	−0.0022 (9)	0.0047 (8)	−0.0038 (9)
C62	0.0579 (14)	0.0531 (14)	0.0741 (18)	0.0181 (11)	−0.0067 (13)	−0.0046 (13)
N7	0.0463 (9)	0.0457 (10)	0.0464 (11)	−0.0019 (8)	0.0051 (8)	0.0002 (9)
C71	0.0320 (9)	0.0353 (10)	0.0415 (12)	−0.0019 (8)	−0.0015 (8)	−0.0067 (9)
C72	0.0594 (14)	0.0597 (15)	0.0436 (13)	−0.0108 (11)	0.0026 (11)	0.0079 (11)
N8	0.0460 (9)	0.0428 (10)	0.0445 (11)	0.0013 (8)	0.0043 (8)	0.0028 (9)
C81	0.0384 (10)	0.0357 (11)	0.0454 (13)	−0.0015 (8)	0.0028 (9)	0.0067 (10)
C82	0.0736 (17)	0.0627 (16)	0.0587 (16)	0.0072 (13)	0.0154 (13)	−0.0113 (13)

Geometric parameters (Å, º)

B1—N1	1.498 (3)	C52—H52A	0.9800
B1—N2	1.501 (3)	C52—H52B	0.9800
B1—N3	1.502 (2)	C52—H52C	0.9800
B1—N4	1.516 (3)	N6—C61	1.129 (2)
N1—C1	1.165 (3)	C61—C62	1.442 (3)
C1—S1	1.589 (2)	C62—H62A	0.9800
N2—C2	1.158 (2)	C62—H62B	0.9800
C2—S2	1.586 (2)	C62—H62C	0.9800
N3—C3	1.153 (2)	N7—C71	1.139 (3)
C3—S3	1.5900 (19)	C71—C72	1.446 (3)
N4—C4	1.161 (2)	C72—H72A	0.9800
C4—S4	1.594 (2)	C72—H72B	0.9800
Li1—N5	1.995 (4)	C72—H72C	0.9800
Li1—N6	2.002 (4)	N8—C81	1.131 (3)
Li1—N8	2.006 (4)	C81—C82	1.456 (4)
Li1—N7	2.013 (4)	C82—H82A	0.9800
N5—C51	1.126 (2)	C82—H82B	0.9800
C51—C52	1.440 (3)	C82—H82C	0.9800
N1—B1—N2	109.56 (18)	H52A—C52—H52C	109.5
N1—B1—N3	109.73 (15)	H52B—C52—H52C	109.5
N2—B1—N3	109.44 (15)	C61—N6—Li1	175.7 (2)
N1—B1—N4	109.94 (16)	N6—C61—C62	179.9 (3)
N2—B1—N4	109.24 (16)	C61—C62—H62A	109.5
N3—B1—N4	108.92 (18)	C61—C62—H62B	109.5
C1—N1—B1	174.95 (19)	H62A—C62—H62B	109.5
N1—C1—S1	179.26 (19)	C61—C62—H62C	109.5
C2—N2—B1	176.46 (18)	H62A—C62—H62C	109.5

N2—C2—S2	179.5 (2)	H62B—C62—H62C	109.5
C3—N3—B1	178.8 (2)	C71—N7—Li1	172.5 (2)
N3—C3—S3	179.6 (2)	N7—C71—C72	179.7 (3)
C4—N4—B1	177.82 (19)	C71—C72—H72A	109.5
N4—C4—S4	179.3 (2)	C71—C72—H72B	109.5
N5—Li1—N6	108.97 (17)	H72A—C72—H72B	109.5
N5—Li1—N8	108.54 (17)	C71—C72—H72C	109.5
N6—Li1—N8	113.70 (17)	H72A—C72—H72C	109.5
N5—Li1—N7	108.48 (17)	H72B—C72—H72C	109.5
N6—Li1—N7	106.15 (17)	C81—N8—Li1	178.0 (2)
N8—Li1—N7	110.86 (17)	N8—C81—C82	179.7 (3)
C51—N5—Li1	175.4 (2)	C81—C82—H82A	109.5
N5—C51—C52	179.3 (2)	C81—C82—H82B	109.5
C51—C52—H52A	109.5	H82A—C82—H82B	109.5
C51—C52—H52B	109.5	C81—C82—H82C	109.5
H52A—C52—H52B	109.5	H82A—C82—H82C	109.5
C51—C52—H52C	109.5	H82B—C82—H82C	109.5