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ISSN 2414-3146

Cyclohexane-1,4-diammonium dithiocyanate

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Received 27 May 2016

Accepted 29 May 2016

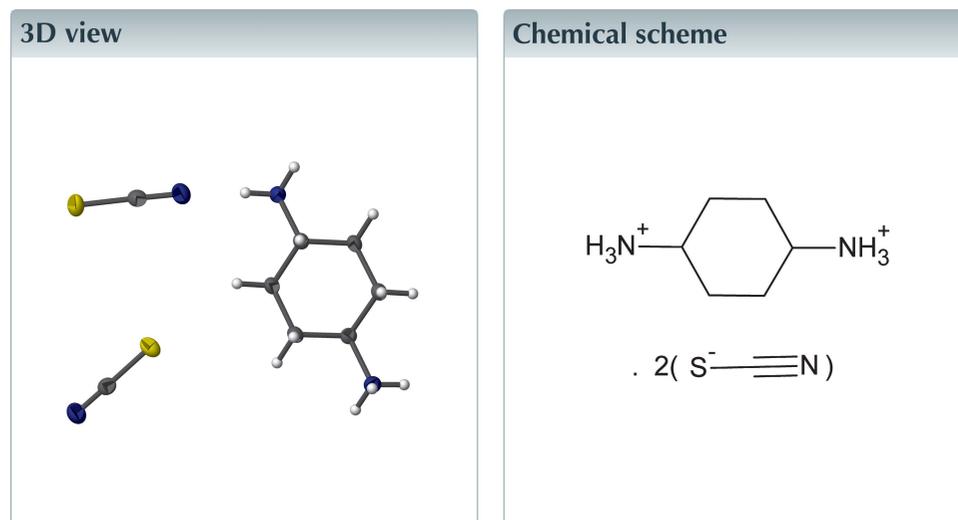
Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; thiocyanate salts; cyclohexane-1,4-diammonium thiocyanate; hydrogen bonds.

CCDC reference: 1482434

Structural data: full structural data are available from iucrdata.iucr.org

In the title salt, $C_6H_{16}N_2^{2+} \cdot 2CNS^-$, the cyclohexane ring adopts a chair conformation. In the crystal, $N-H \cdots N$ hydrogen bonds enclose $R_4^2(8)$ rings involving two N atoms from the cyclohexane-1,4-diammonium cations as donors with the N atoms of two thiocyanate anions as acceptors. The crystal structure is further stabilized by intermolecular $N-H \cdots S$ hydrogen bonds that combine with these contacts to form a three-dimensional network.



Structure description

Thiocyanate salt systems have numerous applications in applied chemistry. For example, a hydrazine/thiocyanate salt was found to act as an excellent solvent for cellulose at room temperature (Hattori *et al.*, 2002). Moreover, incorporation of thiocyanate anions into imidazolium or pyridinium cations produces ionic liquids (Pringle *et al.*, 2002). In addition, a thiocyanate salt of guanidine was recently found to act as a plasticizer for rheological solutions (Selling *et al.*, 2013). In this context we report here the synthesis and crystal structure of the title compound.

As shown in Fig. 1, the cyclohexane ring of the title compound adopts a chair conformation with puckering parameters $Q_T = 0.594$ (2) Å, $\theta = 0.00$ (19)° and $\varphi = 206$ (13)°. The lengths of the equatorial C–N(H₃) bonds in the cyclohexane ring are normal [N1–C1 = 1.502 (2) and N2–C4 = 1.502 (2) Å]. In the two thiocyanate anions, the lengths of the C–S and C≡N bonds are also within normal ranges [S1–C7 = 1.6344 (19), S2–C8 = 1.636 (2), C7–N3 = 1.174 (3), and C8–N4 = 1.167 (3) Å].

In the crystal, N1–H1A···N4, N1–H1B···N3, and N2–H2B···N4, N2–H2C···N3, hydrogen bonds enclose $R_4^2(8)$ rings involving two H atoms from each of the different N atoms of separate cyclohexane-1,4-diammonium cations as donors with the N atoms of

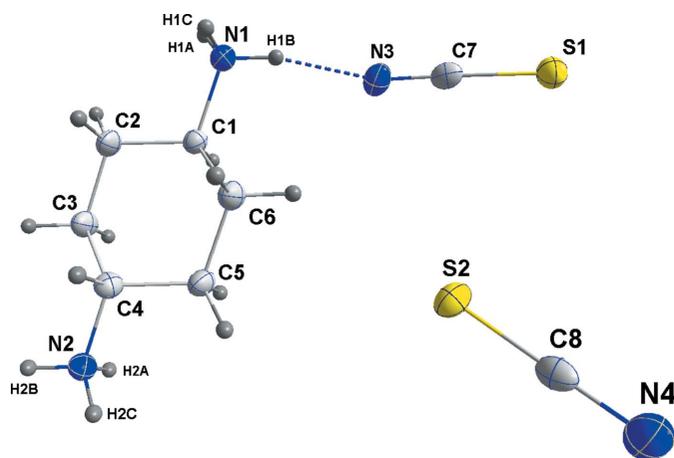


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids.

the two thiocyanate anions as acceptors. Additional intermolecular N1–H1C···S2 and N2–H2A···S1 hydrogen bonds mean that both of the N atoms of the cations are trifurcated donors and these combine with the N–H···N contacts to form a three-dimensional network (Table 1, Fig. 2).

Synthesis and crystallization

The title compound was obtained as an unexpected product in a very good yield (81%) from an attempted multi-component reaction in which phenylacetyl chloride (155 mg, 1 mmol), cyclohexane-1,4-diamine (114 mg, 1 mmol) and potassium thiocyanate (97 mg, 1 mmol) in 30 ml ethanol were refluxed for 5 h. The solid product was collected by filtration, dried under vacuum and recrystallized from ethanol to afford good quality crystals suitable for X-ray diffraction.

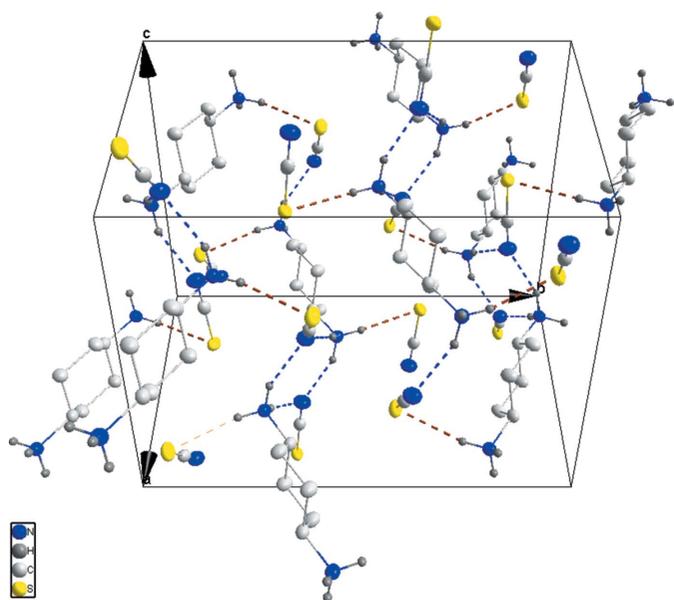


Figure 2
View of the molecular packing and the hydrogen bonding of the title compound.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···N4 ⁱ	0.91	2.04	2.890 (2)	156
N1–H1B···N3	0.91	2.00	2.880 (2)	163
N1–H1C···S2 ⁱⁱ	0.91	2.45	3.3511 (16)	173
N2–H2A···S1 ⁱⁱⁱ	0.91	2.47	3.3621 (16)	169
N2–H2B···N4 ^{iv}	0.91	2.06	2.933 (2)	160
N2–H2C···N3 ^v	0.91	2.08	2.931 (2)	156

Symmetry codes: (i) *x*, *y*, *z* – 1; (ii) –*x* + 1, –*y* + 1, –*z* + 1; (iii) *x* – 1, –*y* + $\frac{1}{2}$, *z* – $\frac{1}{2}$; (iv) *x* – 1, *y*, *z* – 1; (v) *x* – 1, *y*, *z*.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₁₆ N ₂ ²⁺ ·2CNS [–]
<i>M_r</i>	232.37
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.2286 (3), 14.9146 (6), 10.4058 (4)
β (°)	111.423 (1)
<i>V</i> (Å ³)	1188.83 (8)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ^{–1})	3.82
Crystal size (mm)	0.23 × 0.19 × 0.11
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.47, 0.67
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	15185, 4260, 3809
<i>R</i> _{int}	0.032
(<i>sin</i> θ / λ) _{max} (Å ^{–1})	0.618
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.101, 1.04
No. of reflections	4260
No. of parameters	130
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{–3})	0.31, –0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* (Sheldrick, 2008a).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Analysis of 2284 reflections with *I*/ σ (*I*) > 13 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008b) showed the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *a* axis. The raw data were processed using the multi-component version of *SAINT* (Bruker, 2015) under control of the two-component orientation file generated by *CELL_NOW*.

Acknowledgements

The support of NSF–MRI Grant No. 1228232 for the purchase of the diffractometer and Tulane University for support of the

Tulane Crystallography Laboratory are gratefully acknowledged.

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full crystallographic data

IUCrData (2016). **1**, x160864 [doi:10.1107/S2414314616008646]

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Cyclohexane-1,4-diammonium dithiocyanate

Crystal data

$C_6H_{16}N_2^{2+} \cdot 2CNS^-$

$M_r = 232.37$

Monoclinic, $P2_1/c$

$a = 8.2286$ (3) Å

$b = 14.9146$ (6) Å

$c = 10.4058$ (4) Å

$\beta = 111.423$ (1)°

$V = 1188.83$ (8) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.298$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 9989 reflections

$\theta = 5.8\text{--}72.3^\circ$

$\mu = 3.82$ mm⁻¹

$T = 150$ K

Prism, colourless

$0.23 \times 0.19 \times 0.11$ mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS
diffractometer

Radiation source: INCOATEC I μ S micro-focus
source

Mirror monochromator

Detector resolution: 10.4167 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2015)

$T_{\min} = 0.47$, $T_{\max} = 0.67$

15185 measured reflections

4260 independent reflections

3809 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 72.4^\circ$, $\theta_{\min} = 5.5^\circ$

$h = -10 \rightarrow 9$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.101$

$S = 1.04$

4260 reflections

130 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

$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.366P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ e Å⁻³

Special details

Experimental. Analysis of 2284 reflections having $I/\sigma(I) > 13$ and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *a* axis. The raw data were processed using the multi-component version of *SAINTE* under control of the two-component orientation file generated by *CELL_NOW*.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.98 - 1.0 Å) while those attached to nitrogen were placed in locations derived from a difference map and their parameters adjusted to give N—H = 0.91 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Refined as a 2-component twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.56447 (18)	0.45162 (11)	0.25836 (16)	0.0221 (3)
H1A	0.5902	0.4406	0.1819	0.033*
H1B	0.6616	0.4431	0.3353	0.033*
H1C	0.5272	0.5092	0.2562	0.033*
N2	-0.06213 (18)	0.29200 (11)	0.27141 (16)	0.0226 (3)
H2A	-0.0251	0.2342	0.2761	0.034*
H2B	-0.1584	0.2997	0.1936	0.034*
H2C	-0.0891	0.3047	0.3468	0.034*
C1	0.4231 (2)	0.38878 (13)	0.26112 (18)	0.0201 (4)
H1	0.4652	0.3259	0.2615	0.024*
C2	0.2610 (2)	0.40194 (14)	0.13238 (19)	0.0247 (4)
H2D	0.2890	0.3899	0.0492	0.030*
H2E	0.2204	0.4648	0.1278	0.030*
C3	0.1169 (2)	0.33831 (13)	0.13575 (19)	0.0248 (4)
H3A	0.0093	0.3491	0.0542	0.030*
H3B	0.1536	0.2754	0.1324	0.030*
C4	0.0802 (2)	0.35377 (12)	0.26759 (19)	0.0207 (4)
H4	0.0400	0.4170	0.2676	0.025*
C5	0.2427 (2)	0.33951 (13)	0.39591 (19)	0.0241 (4)
H5A	0.2830	0.2767	0.3992	0.029*
H5B	0.2154	0.3509	0.4796	0.029*
C6	0.3865 (2)	0.40364 (13)	0.39237 (19)	0.0242 (4)
H6A	0.3493	0.4664	0.3959	0.029*
H6B	0.4942	0.3930	0.4738	0.029*
S1	1.10256 (6)	0.41245 (3)	0.75714 (5)	0.02824 (16)
N3	0.8593 (2)	0.38720 (13)	0.48827 (18)	0.0313 (4)
C7	0.9609 (2)	0.39952 (12)	0.6002 (2)	0.0224 (4)
S2	0.60809 (6)	0.34284 (3)	0.76345 (5)	0.02790 (16)
N4	0.6417 (2)	0.36365 (14)	1.03977 (18)	0.0352 (4)
C8	0.6273 (2)	0.35421 (13)	0.9248 (2)	0.0240 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0216 (7)	0.0231 (8)	0.0213 (7)	-0.0007 (6)	0.0073 (6)	0.0014 (6)
N2	0.0228 (7)	0.0224 (8)	0.0234 (8)	-0.0016 (6)	0.0094 (6)	-0.0013 (6)
C1	0.0225 (8)	0.0187 (8)	0.0187 (9)	-0.0012 (7)	0.0070 (7)	0.0002 (7)
C2	0.0254 (9)	0.0302 (10)	0.0167 (9)	-0.0037 (7)	0.0055 (7)	0.0022 (7)
C3	0.0254 (9)	0.0301 (11)	0.0183 (9)	-0.0054 (7)	0.0073 (7)	-0.0031 (7)
C4	0.0230 (8)	0.0182 (8)	0.0214 (9)	-0.0027 (7)	0.0086 (7)	-0.0014 (7)
C5	0.0266 (9)	0.0280 (10)	0.0177 (9)	-0.0046 (7)	0.0080 (7)	0.0009 (7)
C6	0.0257 (9)	0.0281 (10)	0.0178 (9)	-0.0055 (7)	0.0069 (7)	-0.0023 (7)
S1	0.0312 (3)	0.0230 (3)	0.0239 (3)	-0.00248 (17)	0.00225 (19)	0.00112 (18)
N3	0.0304 (8)	0.0382 (10)	0.0241 (9)	0.0031 (7)	0.0085 (7)	0.0010 (7)
C7	0.0237 (8)	0.0199 (9)	0.0262 (10)	0.0029 (7)	0.0120 (7)	0.0016 (7)
S2	0.0386 (3)	0.0239 (3)	0.0236 (3)	0.00396 (18)	0.0142 (2)	0.00093 (18)
N4	0.0347 (9)	0.0459 (11)	0.0252 (9)	0.0026 (8)	0.0111 (7)	-0.0011 (8)
C8	0.0213 (8)	0.0226 (9)	0.0282 (10)	0.0011 (7)	0.0091 (7)	0.0029 (8)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.502 (2)	C3—C4	1.526 (2)
N1—H1A	0.9100	C3—H3A	0.9900
N1—H1B	0.9100	C3—H3B	0.9900
N1—H1C	0.9100	C4—C5	1.520 (2)
N2—C4	1.502 (2)	C4—H4	1.0000
N2—H2A	0.9100	C5—C6	1.533 (2)
N2—H2B	0.9100	C5—H5A	0.9900
N2—H2C	0.9100	C5—H5B	0.9900
C1—C6	1.518 (2)	C6—H6A	0.9900
C1—C2	1.519 (2)	C6—H6B	0.9900
C1—H1	1.0000	S1—C7	1.6344 (19)
C2—C3	1.529 (2)	N3—C7	1.174 (3)
C2—H2D	0.9900	S2—C8	1.636 (2)
C2—H2E	0.9900	N4—C8	1.167 (3)
C1—N1—H1A	109.5	C4—C3—H3A	109.7
C1—N1—H1B	109.5	C2—C3—H3A	109.7
H1A—N1—H1B	109.5	C4—C3—H3B	109.7
C1—N1—H1C	109.5	C2—C3—H3B	109.7
H1A—N1—H1C	109.5	H3A—C3—H3B	108.2
H1B—N1—H1C	109.5	N2—C4—C5	109.56 (14)
C4—N2—H2A	109.5	N2—C4—C3	110.06 (14)
C4—N2—H2B	109.5	C5—C4—C3	111.69 (15)
H2A—N2—H2B	109.5	N2—C4—H4	108.5
C4—N2—H2C	109.5	C5—C4—H4	108.5
H2A—N2—H2C	109.5	C3—C4—H4	108.5
H2B—N2—H2C	109.5	C4—C5—C6	109.30 (15)
N1—C1—C6	109.60 (14)	C4—C5—H5A	109.8

N1—C1—C2	109.84 (14)	C6—C5—H5A	109.8
C6—C1—C2	112.07 (15)	C4—C5—H5B	109.8
N1—C1—H1	108.4	C6—C5—H5B	109.8
C6—C1—H1	108.4	H5A—C5—H5B	108.3
C2—C1—H1	108.4	C1—C6—C5	109.82 (15)
C1—C2—C3	109.77 (15)	C1—C6—H6A	109.7
C1—C2—H2D	109.7	C5—C6—H6A	109.7
C3—C2—H2D	109.7	C1—C6—H6B	109.7
C1—C2—H2E	109.7	C5—C6—H6B	109.7
C3—C2—H2E	109.7	H6A—C6—H6B	108.2
H2D—C2—H2E	108.2	N3—C7—S1	177.77 (18)
C4—C3—C2	109.65 (15)	N4—C8—S2	179.0 (2)
N1—C1—C2—C3	-179.67 (14)	N2—C4—C5—C6	-179.20 (14)
C6—C1—C2—C3	-57.6 (2)	C3—C4—C5—C6	58.6 (2)
C1—C2—C3—C4	56.5 (2)	N1—C1—C6—C5	-179.85 (14)
C2—C3—C4—N2	179.60 (15)	C2—C1—C6—C5	57.9 (2)
C2—C3—C4—C5	-58.5 (2)	C4—C5—C6—C1	-57.1 (2)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...N4 ⁱ	0.91	2.04	2.890 (2)	156
N1—H1B...N3	0.91	2.00	2.880 (2)	163
N1—H1C...S2 ⁱⁱ	0.91	2.45	3.3511 (16)	173
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N2—H2C...N3 ^v	0.91	2.08	2.931 (2)	156

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+1, -y+1, -z+1$; (iii) $x-1, -y+1/2, z-1/2$; (iv) $x-1, y, z-1$; (v) $x-1, y, z$.