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Key indicators

Single-crystal X-ray study

$T = 113\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.043

wR factor = 0.131

Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

3,10-*C-meso*-2,5,5,7,9,12,12,14-Octamethyl-1,8-diaza-4,11-diazoniacyclotetradecane bis(thiocyanate)

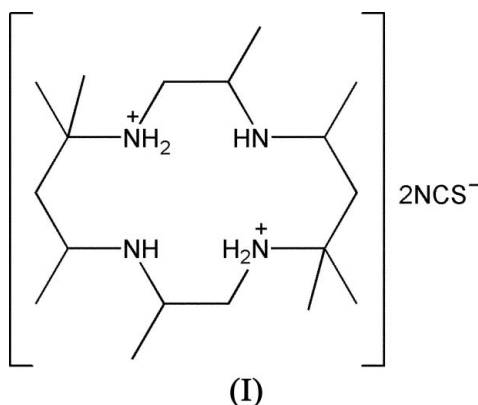
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The title compound, $\text{C}_{18}\text{H}_{42}\text{N}_4^{2+} \cdot 2\text{CNS}^-$, contains diprotonated cations located about centres of inversion, with charge balance provided by thiocyanate anions. Intermolecular $\text{N}-\text{H} \cdots \text{N}$ and $\text{N}-\text{H} \cdots \text{S}$ hydrogen bonds are formed in the crystal structure, which comprises columns of macrocyclic cations that define channels in which the thiocyanate anions reside.

Comment

The title compound, (I), was characterized during studies of ligands of this type and their transition-metal complexes (Roy *et al.*, 2001, 2006).



The cation of (I) (Fig. 1) is located about a centre of inversion and is protonated at atoms N4 and N8. Charge balance is provided by two thiocyanate anions. The geometric parameters (Table 1) are in accord with related species (Drew & Mok, 1987; Roy *et al.*, 2001).

Each of the $\text{N}-\text{H}$ groups is involved in hydrogen bonding. Atom N4 is involved in an intramolecular interaction with atom N1ⁱ [symmetry code: (i) $1 - x, 1 - y, 1 - z$], while the remaining $\text{N}-\text{H}$ groups form interactions with thiocyanate anions (Table 2). Both ends of the thiocyanate anion are connected to cations *via* $\text{N}-\text{H} \cdots \text{N}$ and $\text{N}-\text{H} \cdots \text{S}$ interactions. The macrocyclic cations are aligned into columns along a , defining channels in which the anions reside (Fig. 2).

Experimental

The compound 3*S*,10*R*-*C-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Curtis *et al.*, 1969), on reduction with NaBH_4 , yields an isomeric mixture of saturated macrocycles, the $\text{Me}_8[14]$ anes, which have been resolved into three distinct isomers (Bembi *et al.*, 1989). One of the isomers, L_B (Bembi *et al.*, 1989), on heating in methanolic solution with KSCN and HCl for

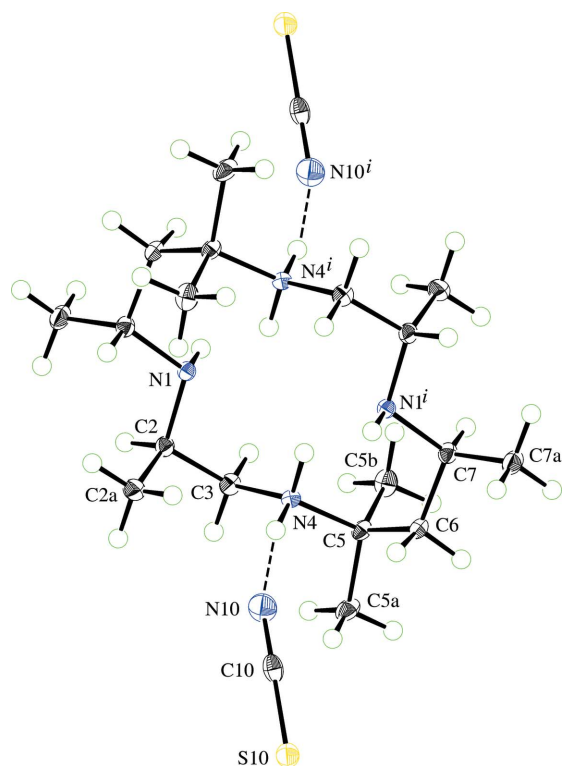


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

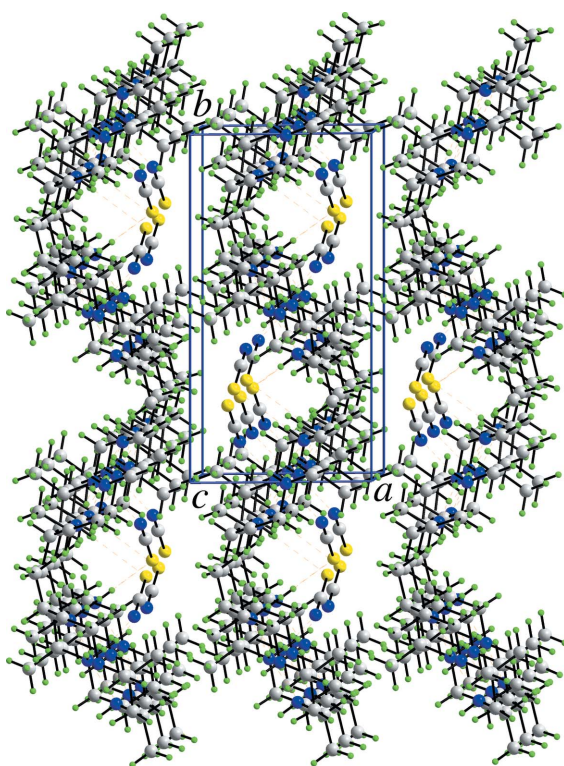


Figure 2
A view of (I) along c (with the origin in the back plane of the unit cell), showing hydrogen bonds as dashed orange lines. Colour code: S atoms are shown in yellow, N atoms in blue, C atoms in grey and H atoms in green.

10 min in the ratio of 1:4:3, followed by cooling and slow evaporation at room temperature for 24 h, produced the colourless and crystalline product $[L_B H_2][SCN]_2$, (I).

Crystal data

$C_{18}H_{42}N_4^{2+} \cdot 2NCS^-$
 $M_r = 430.72$
Monoclinic, $P2_1/c$
 $a = 7.804$ (4) Å
 $b = 14.490$ (5) Å
 $c = 11.057$ (6) Å
 $\beta = 107.74$ (2)°
 $V = 1190.8$ (10) Å³

$Z = 2$
 $D_x = 1.201$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 113$ (2) K
Block, colourless
 $0.52 \times 0.31 \times 0.19$ mm

Data collection

Rigaku R-Axis SPIDER
diffractometer
 ω scans
Absorption correction: numerical
(Katayama, 1986; Paturle & Coppens, 1988)
 $T_{min} = 0.882$, $T_{max} = 0.956$

6518 measured reflections
2330 independent reflections
1986 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.027$
 $\theta_{max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.131$
 $S = 1.11$
2330 reflections
139 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.6204P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.44$ e Å⁻³
 $\Delta\rho_{min} = -0.34$ e Å⁻³

H atoms treated by a mixture of independent and constrained refinement

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------------------|-------------|-------------|-------------|
| N1—C2 | 1.479 (2) | C5—C5b | 1.523 (3) |
| N1—C7 ⁱ | 1.490 (2) | C5—C6 | 1.537 (3) |
| N4—C3 | 1.494 (2) | C6—C7 | 1.529 (3) |
| N4—C5 | 1.524 (2) | C7—C7a | 1.528 (3) |
| C2—C2a | 1.520 (3) | N10—C10 | 1.162 (3) |
| C2—C3 | 1.517 (3) | C10—S10 | 1.653 (2) |
| C5—C5a | 1.527 (3) | | |
| C2—N1—C7 ⁱ | 113.79 (14) | N10—C10—S10 | 178.97 (19) |
| C3—N4—C5 | 116.28 (14) | | |

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|----------|--------------|--------------|----------------|
| N4—H4a \cdots N10 | 0.87 (2) | 2.04 (2) | 2.898 (3) | 168 (2) |
| N4—H4b \cdots N1 ⁱ | 0.97 (2) | 2.02 (2) | 2.842 (3) | 141 (2) |
| N1—H1a \cdots S10 ⁱⁱ | 0.89 (2) | 2.74 (2) | 3.609 (3) | 169 (2) |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.98 (methyl H), 0.99 (methylene H) and 1.00 Å (methine H), and with $U_{iso}(H) = 1.2U_{eq}(C)$ for methine and methylene H atoms or $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. H atoms bound to N atoms were located in a difference Fourier map and refined freely with isotropic displacement parameters.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

structure: *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Crystal Impact, 2006); software used to prepare material for publication: *SHELXL97*.

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