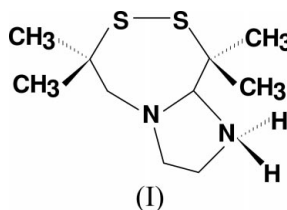


6,6,9,9-Tetramethyl-1,2,5,6,9,9a-hexahydroimidazo[2,1-*d*][1,2,5]dithiazepin-1-ium triiodideTrevor W. Hambley,^a
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Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.013 \text{ \AA}$
R factor = 0.041
wR factor = 0.033
Data-to-parameter ratio = 12.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The crystal structure of the title compound, $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_2^+\cdot\text{I}_3^-$, has been obtained from 294 K single-crystal X-ray diffraction data. The triiodide ion is 3.617 (8) \AA from the protonated amine of the heterocycle.

Comment

Growing interest in the potential of radioisotopes ^{186}Re and ^{188}Re for tumour-targeting radiotherapy (Nicolini & Mazzi, 1999) has led to the investigation of suitable ligands for complexation. In previous papers (Jackson *et al.*, 1993, 2001; Hambley *et al.*, 1995), we have described the preparation of several lipophilic rhenium–diamino–dithiolate complexes and their crystal structures. We report here the crystal structure of the protonated form of a ligand suitable for complexation with Re isotopes. The ligand is 6,6,9,9-tetramethyl-1,2,5,6,9,9a-hexahydroimidazo[2,1-*d*][1,2,5]dithiazepine, (I), and is reported as the triiodide salt.The closest contact between the heterocyclic cation and its counter-ion is 3.617 (8) \AA , *i.e.* between I1 and the protonated N1 atom. The Cambridge Structural Database (Allen & Kennard, 1993) has 13 contacts between iodine and a protonated secondary amine, for which the mean distance is 3.649 \AA and the shortest is 3.437 \AA . In addition to an electrostatic interaction, there may be weak hydrogen bonding between the triiodide and the protonated nitrogen site of the heterocyclic cation.The disulfide S–S bond of 1.983 (4) \AA in the title compound is significantly shorter than the mean length of 2.038 \AA obtained from the Cambridge Structural Database. The shortest disulfide bond length in the Cambridge Structural Database is 1.950 \AA .As Fig. 2 indicates, the heterocyclic cation and its counter-ion pack in channels running parallel to the *a* axis of the unit cell and are separated by the length of that axis.

Experimental

For the preparation of the title compound, 6,6,9,9-hexamethylhexahydroimidazo[2,1-*d*][1,2,5]dithiazepine (4.85 g) and methyl iodide (3.64 g, 1.3 molar equivalent, not distilled) in 20 ml of ethyl alcohol

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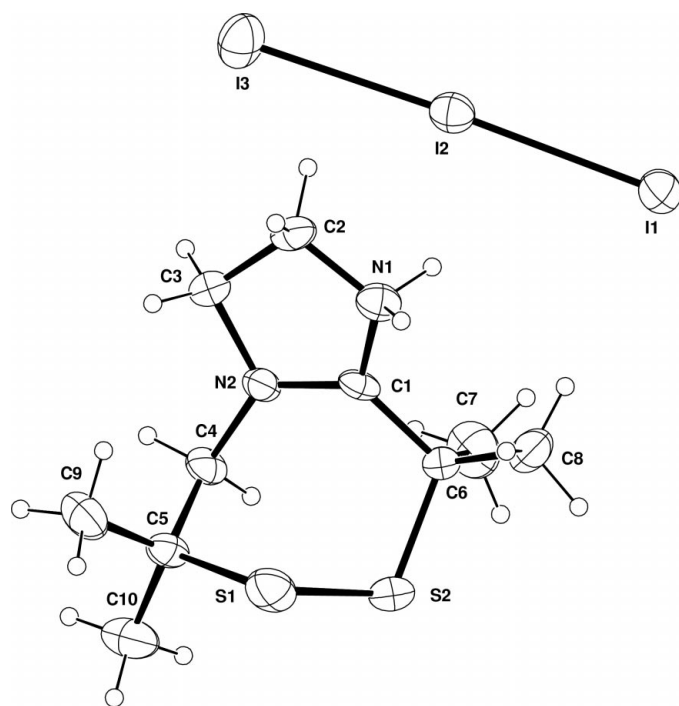


Figure 1
A view of the triiodide salt of (I) with displacement ellipsoids shown at the 20% probability level.

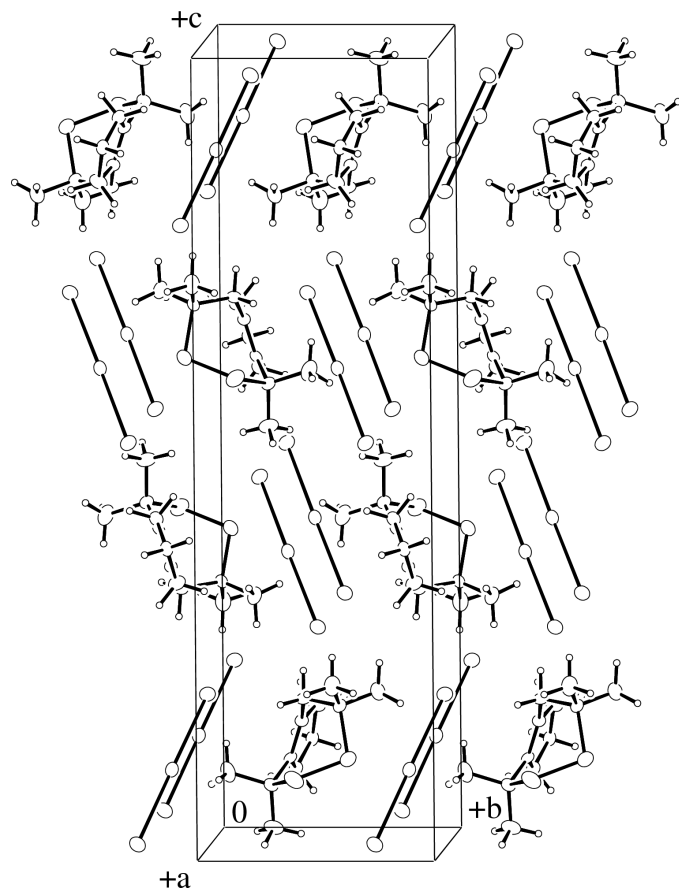


Figure 2
A view of the packing for (I).

were refluxed for 3 h. After cooling, crystals were collected by filtration and washed with diethyl ether. Yield 6.17 g, m.p. 466–468 K.

Crystal data

$C_{10}H_{20}N_2S_2^+ \cdot I_3^-$
 $M_r = 613.11$
 Monoclinic, $P2_1/c$
 $a = 8.3334$ (9) Å
 $b = 8.080$ (2) Å
 $c = 27.274$ (6) Å
 $\beta = 93.57$ (1)°
 $V = 1832.9$ (5) Å³
 $Z = 4$

$D_x = 2.222$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 8.1$ – 12.1 °
 $\mu = 5.33$ mm⁻¹
 $T = 294$ (1) K
 Prism, brown
 $0.30 \times 0.22 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – θ scans
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.330$, $T_{\max} = 0.768$
 4236 measured reflections
 3218 independent reflections
 1918 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 25.0$ °
 $h = -9 \rightarrow 9$
 $k = -1 \rightarrow 9$
 $l = -1 \rightarrow 32$
 3 standard reflections every 100 reflections
 frequency: 60 min
 intensity decay: 2.6%

Refinement

Refinement on F
 $R = 0.041$
 $wR = 0.033$
 $S = 1.86$
 1918 reflections
 154 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.82$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.86$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

I1–I2	2.906 (1)	N1–C1	1.29 (1)
I2–I3	2.916 (1)	N1–C2	1.44 (1)
S1–S2	1.983 (4)	N2–C1	1.33 (1)
S1–C5	1.83 (1)	N2–C3	1.50 (1)
S2–C6	1.830 (10)	N2–C4	1.44 (1)
I1–I2–I3	178.05 (4)	C1–N2–C3	110.4 (9)
S2–S1–C5	102.5 (4)	C1–N2–C4	127.6 (9)
S1–S2–C6	107.2 (4)	C3–N2–C4	121.8 (9)
C1–N1–C2	115.0 (9)		

Table 2

Selected contact distances (Å).

I1...N1 ⁱ	3.617 (8)	I2...N1 ^{iv}	3.861 (8)
I1...N1 ⁱⁱ	3.858 (8)	I2...C2 ^{iv}	3.931 (8)
I1...C2 ⁱⁱ	3.985 (9)	I3...C3 ^v	3.912 (10)
I1...S2 ⁱⁱⁱ	3.981 (3)		

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976; Hall *et al.*, 1999); software used to prepare material for publication: *TEXSAN*.

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