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Intramolecular cyclization of 4,7-bis(2-bromoacetyl)-1-thia-4,7-diazacyclononane

Alexander J. Blake,[a]* Vito Lippolis[b] and Martin Schröder[a]

[a]School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England, and [b]Dipartimento di Chimica Inorganica ed Analitica, Università degli Studi di Cagliari, Complesso Universitario di Monserrato, SS 554 bivio per Sestu, 09042 Monserrato (CA), Italy
Correspondence e-mail: a.j.blake@nottingham.ac.uk

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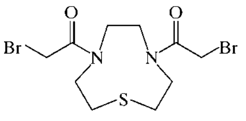
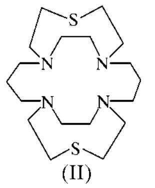
The reaction of 1-thia-4,7-diazacyclononane with bromoacetyl bromide in $CHCl_3$ affords the unexpected salt 4-(2-bromoacetyl)-8-oxo-1-thionia-4,7-diazabicyclo[5.2.2]undecane bromide, $C_{10}H_{16}BrN_2O_2S^+\cdot Br^-$. Two units of the salt are linked by S···Br contacts about a crystallographic inversion centre, thus forming dimers that are linked by Br···Br contacts into extended ribbons. S···O contacts between these ribbons generate a two-dimensional sheet.

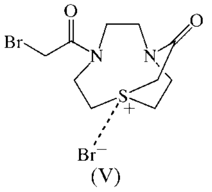
Comment

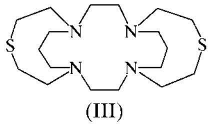
The design and synthesis of macrobicyclic and macrotricyclic ligands including cages and cryptands, and the preparation of their metal complexes, are topics of current interest (Sargeson, 1996; Ingham *et al.*, 2002). Many of the polymacrocyclic ligands described so far, some of them based on a cyclam framework, have been used extensively for the preparation of metal complexes of high kinetic and thermodynamic stability, such complexes often exhibiting specific coordination and redox properties. Two major synthetic approaches are normally used in the preparation of these types of macrocyclic systems, the first being direct synthesis based on conventional organic reactions and metal-ion template synthesis (Ingham *et al.*, 2002). The second procedure involves the preparation of a complexed metal ion within which the coordinated ligand can undergo further reaction.

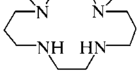
With the aim of preparing new mixed-donor macrobicyclic ligands containing the 1-thia-4,7-diazacyclononane ([9]-aneN_2S) framework, we sought to use the corresponding 2-bromoacetyl derivative, (I), as a suitable claw-like precursor. Three macropolycyclic systems containing the [9]aneN_2S framework, namely (II), (III) and (IV), have already been reported. Compound (II) was synthesized by reaction of cyclam with four equivalents of chloroacetyl chloride, followed by ring closure with Na_2S and subsequent reduction with BH_3 (Ingham *et al.*, 2002). Compound (III) was prepared by reacting [9]aneN_2S with 1,3-bis(2-chloroacetamido)-propane, followed by reduction with BH_3 and reaction of the resulting macrobicyclic system with $(BrCH_2CH_2)_2S$ (Ingham *et al.*, 2002). The alternative template method was employed in the preparation of (IV), starting from the Cu^{II} complex of 4,7-bis(3-aminopropyl)-1-thia-4,7-diazacyclononane (Fortier & McAuley, 1989). In order to prepare (I), we reacted [9]aneN_2S with two equivalents of bromoacetyl bromide and pyridine in $CHCl_3$, and the residue obtained after removal of the solvent was dissolved in diethyl ether. A white crystalline solid, having elemental analysis consistent with (I), separated from the Et_2O solution. Interestingly, this product was soluble in water and insoluble in $CHCl_3$, suggesting that the compound isolated was not (I). Single crystals were grown by diffusion of Et_2O vapour into a dimethylformamide (DMF) solution of the product and X-ray diffraction analysis was undertaken to ascertain its nature.


(I)


(II)


(V)


(III)


(IV)

The structure determination revealed the formation of the unexpected salt 4-(2-bromoacetyl)-8-oxa-1-thionia-4,7-diaza-bicyclo[5.2.2]undecane bromide, (V) (Fig. 1), as the result of

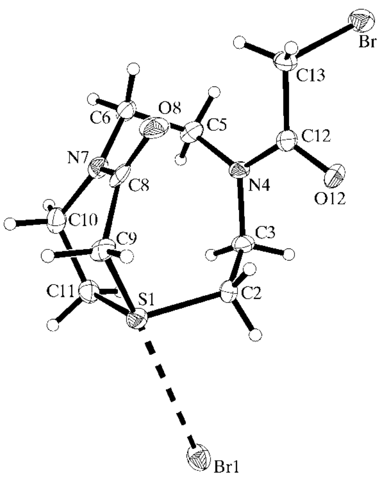


Figure 1
A view of (V), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

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an intramolecular cyclization of (I), where a bromoacetyl pendant arm undergoes nucleophilic attack by the S donor of the [9]aneN$_2$S framework. The resulting bicyclic sulfonium cation in this salt incorporates fused six- and nine-membered rings, the former adopting a boat conformation with sulfonium atom S1 at the bridgehead. Atom S1 interacts with the bromide counter-ion in the same asymmetric unit [S1$\cdots$Br1 = 3.4127 (14) Å; Fig. 1]. The acetyl bridge formed between atoms N7 and S1 causes the [9]aneN$_2$S framework to assume a [234] conformation, in contrast to the [333] conformation normally observed for [9]aneN$_2$S and its pendant-arm derivatives within their metal-ion complexes (Danks *et al.*, 1998; Arca *et al.*, 2003). The S1—C bond lengths and the C—S1—C angles (Table 1) are typical for this type of compound and are comparable to those observed for the bicyclic sulfonium salt [C$_6$H$_{11}$S$_3$]BF$_4$, obtained by oxidation of 1,4,7-trithiacyclononane ([9]aneS$_3$) with Au$^{\rm III}$, a process that proceeds *via* C—H bond cleavage and transannular S—C bond formation (Taylor *et al.*, 1991).

Two units of salt (V) are linked about a crystallographic inversion centre, forming dimers *via* S$\cdots$Br contacts [S1$\cdots$Br1$^{\rm i}$ = 3.8676 (14) Å; symmetry code: (i) $-x, 1-y, -z$]. These contacts are longer than the S1$\cdots$Br1 contact within the asymmetric unit (Fig. 2), and thus two sulfonium cations and two bromide anions are located at the opposite corners of a parallelogram [S1$\cdots$Br1$\cdots$S1$^{\rm i}$ = 68.94 (3)° and Br1$\cdots$S1$\cdots$Br1$^{\rm i}$ = 111.06 (3)°]. Dimers of (V) are joined *via* Br$\cdots$Br1 contacts of 3.6348 (9) Å between bromide anions and Br atoms belonging to unreacted bromoacetyl pendant arms [Br$^{\rm ii}\cdots$Br1$\cdots$S1$^{\rm i}$ = 167.77 (3)°; symmetry code: (ii) $1-x, 1-y, 1-z$], thus forming ribbons that run along the [101] direction. Ribbons of this type are joined *via* S$\cdots$O contacts of 3.0512 (4) Å, forming two-dimensional sheets (Fig. 3). The use of (V) as an intermediate for the asymmetric functionalization of [9]aneN$_2$S is under investigation.

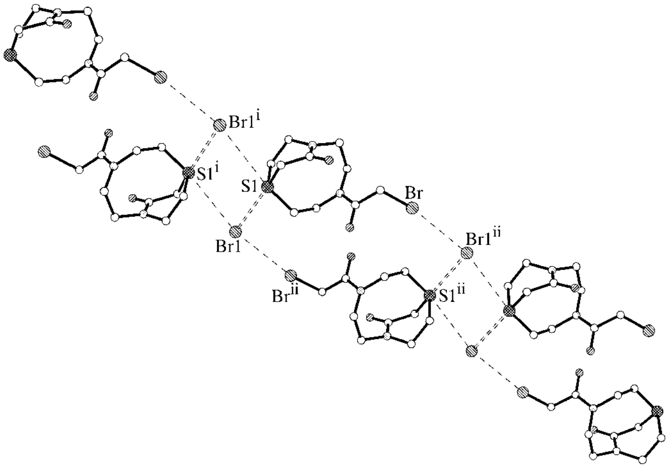

Figure 2
A view of part of a ribbon running along the [101] direction and comprising dimers of salt (V) interacting *via* Br$\cdots$Br contacts. [Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$.]

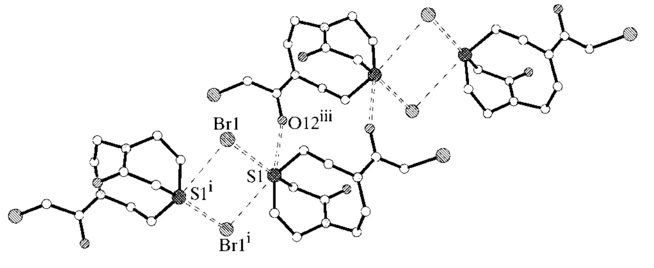

Figure 3
A view of part of an extended two-dimensional sheet comprising the ribbons shown in Fig. 2 joined by S$\cdots$O contacts. [Symmetry codes: (i) $-x, 1-y, -z$; (iii) $x-1, y, z-1$.]

Experimental

A solution of 2-bromoacetyl bromide (2.84 g, 14.08 mmol) and pyridine (1.11 g, 14.08 mmol) in CHCl$_3$ (20 ml) was added dropwise over a period of 30 min to a solution of 1-thia-4,7-diazacyclononane (0.97 g, 6.64 mmol) in CHCl$_3$ (15 ml) cooled to 273 K. The resulting reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was taken up in diethyl ether. On standing, a white crystalline solid separated out. Crystals suitable for X-ray diffraction analysis were grown by diffusion of Et$_2$O vapour into a DMF solution of the product. Analysis found: C 30.50, H 4.12, N 7.18%; calculated for C$_{10}$H$_{16}$Br$_2$N$_2$O$_2$S: C 30.95, H 4.15, N 7.22%. ^{13}C NMR (D$_2$O, 75.47 MHz, 298 K): δ 27.2, 32.5, 38.8, 39.6, 44.4, 47.3, 47.8, 50.0, 166.6. 171.8.

Crystal data

C$_{10}$H$_{16}$BrN$_2$O$_2$S$^+$·Br$^-$
M_r = 388.13
Triclinic, $P\overline{1}$
a = 7.2655 (10) Å
b = 9.5032 (13) Å
c = 10.0740 (15) Å
α = 86.665 (12)°
β = 75.553 (13)°
γ = 83.068 (10)°
V = 668.36 (17) Å^3

Z = 2
D_x = 1.929 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 56 reflections
θ = 12.5–15°
μ = 6.21 mm^{-1}
T = 150 (2) K
Block, colourless
0.52 × 0.25 × 0.19 mm

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–θ scans
Absorption correction: ψ scan (*X-RED*; Stoe & Cie, 1997)
$T_{\rm min}$ = 0.112, $T_{\rm max}$ = 0.308
2374 measured reflections
2360 independent reflections
2109 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.059
$\theta_{\rm max}$ = 25.1°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -2 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.126
S = 1.05
2360 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 2.906P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 1.17 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.831 (5)	S1—C11	1.803 (5)
S1—C9	1.819 (5)		
C2—S1—C9	104.1 (2)	C9—S1—C11	98.7 (2)
C2—S1—C11	106.0 (2)		

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H atoms were placed geometrically and thereafter treated as riding on their parent C atoms [C—H = 0.99 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)].

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *enCIFer* (CCDC, 2003) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1685). Services for accessing these data are described at the back of the journal.

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