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Key indicators

Single-crystal X-ray study

$T = 153$ K

Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å

R factor = 0.028

wR factor = 0.071

Data-to-parameter ratio = 14.7

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

A thiophene-based azacryptand Mannich base: 15,35-dipropyl-2,5,8,22,25,28-hexaoxa-12,18,32,38-tetra-thia-15,35-diazapentacyclo[29.5.5.5.0.0]tetraconta-1(37),9(13),10,17(21),19,29(33),30,39-octaene

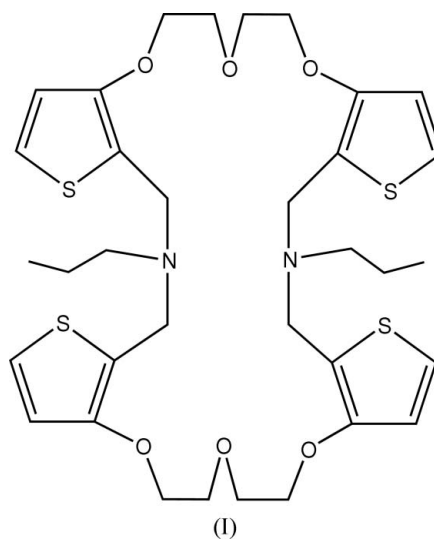
The molecule of the title compound, $\text{C}_{34}\text{H}_{46}\text{N}_2\text{O}_6\text{S}_4$ is composed of four thiophene rings bridged by two $-\text{O}(\text{CH}_2)_2\text{O}-$ and two $-\text{CH}_2(\text{NC}_2\text{H}_5)\text{CH}_2-$ chains. The macrocyclic molecule possesses a center of symmetry. In the crystal structure, the molecules are bridged by $\text{C}-\text{H}\cdots\text{O}$ interactions, forming chains along the a axis.

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Comment

The preparation of cryptand-like structures, incorporating four thiophene rings, was previously described by Chaffin *et al.* (2001, 2002). The title compound is the first of a range of four thiophene-based azacryptand Mannich bases. The macrocycle incorporates six O and two N donor atoms. The coordination chemistry of aza and mixed oxa-aza macrocycles containing different pendant arms attached to the aza centers has attracted the attention of many researchers over the past twenty years (Tei *et al.*, 2000; Wainwright, 1997; Bernhardt & Lawrance, 1990; Gokel, 1992; Hancock *et al.*, 1996; Hambley *et al.*, 2001; Buschmann & Schollmeyer, 2000; Dietrich *et al.*, 1969). These ligands can exhibit remarkable metal-ion selectivity and show specific complexation behavior, forming metal complexes with unusual structures (references as above, together with Laufer, 1987; Parker & Williams, 1996). Macrocyclic crown ethers and other ionophores can bind cations (Gokel & Durst, 1976), anions and small neutral organic molecules (Kellogg, 1984).



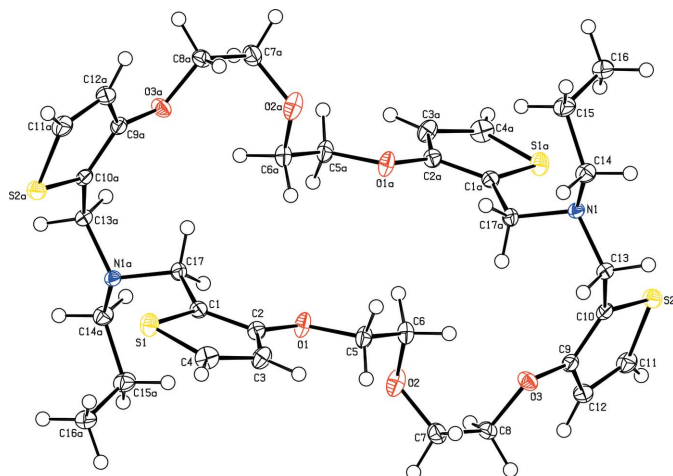


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (a) $-x, -y, 1 - z$.]

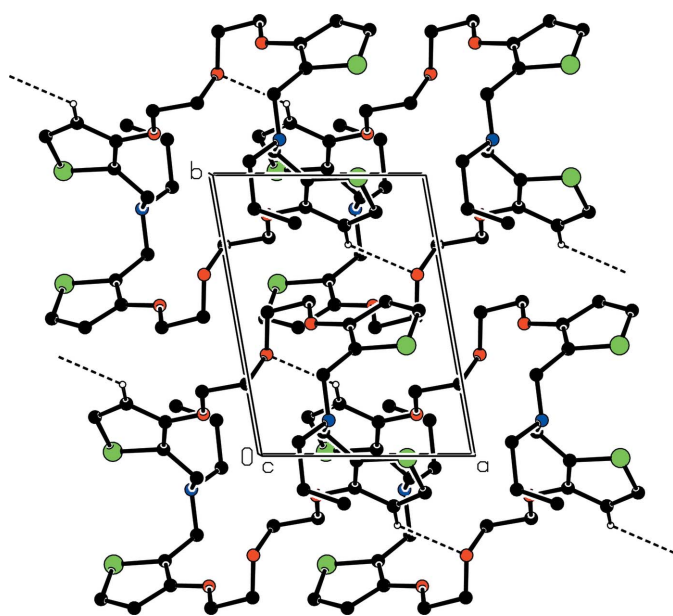


Figure 2

The molecular packing of compound (I), with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

thiophene rings is planar, and opposite rings are parallel by symmetry. The S1 and S2 rings form a dihedral angle of $82.50(3)^\circ$. The cross-molecule distances between the thiophene rings are $S1 \cdots S1^i = 11.323(2) \text{ \AA}$ and $S2 \cdots S2^i = 14.735(4) \text{ \AA}$ [symmetry code: (i) $-x, -y, 1 - z$]. The large separation of the S1 and S2 thiophene rings [$S1 \cdots S2 = 12.567(3) \text{ \AA}$], and the relative proximity of the S1 and S2ⁱ rings [$S1 \cdots S2^i = 3.8412(12) \text{ \AA}$], means that the O and N atoms do not lie in the same plane. The largest cross-cavity distances are $N1 \cdots N1^i = 10.223(3) \text{ \AA}$, and $O3 \cdots O3^i = 10.052(4) \text{ \AA}$. The macrocyclic cavity can be divided into three small cavities defined respectively by least-squares planes

through the N1, O2, O3 and O1ⁱ donor atoms for the first, through N1ⁱ, O2ⁱ, O3ⁱ and O1 for the second, and through O1, O2, O1ⁱ and O2ⁱ for the third. The two NO₃ planes are parallel and form a dihedral angle of $47.61(5)^\circ$ with the third plane. The largest cross-cavity distances for these three smaller cavities are $N1 \cdots O2 = N1^i \cdots O2^i = 5.422(2) \text{ \AA}$, $O1 \cdots O3^i = O1^i \cdots O3 = 5.656(2) \text{ \AA}$, $O1 \cdots O1^i = 4.806(3) \text{ \AA}$, and $O2 \cdots O2^i = 6.425(3) \text{ \AA}$. The $N1 \cdots S1^i$ and $N1 \cdots S2$ distances are $3.0851(18) \text{ \AA}$ and $3.4439(17) \text{ \AA}$, respectively. The $N1 \cdots S2$ distance is equal to the sum of the van der Waals radii (3.45 \AA), whereas the $N1 \cdots S1^i$ distance is much shorter, and also considerably shorter than the non-bonded $N \cdots S$ interaction reported by Halfpenny & Sloman (2000) and Koziol *et al.* (1988). Consistent with this are the smaller S1–C1–C17 and S2–C10–C13 angles, compared with C2–C1–C17 and C9–C10–C13, and the smaller torsion angle S2–C10–C13–N1, compared with C9–C10–C13–N1. Some distortion in the thiophene ring bond lengths and angles is observed in many substituted thiophene compounds, the most obvious effect being the asymmetric nature of the S–C bonds (Koziol *et al.*, 1988). In the present compound the rings associated with the $S \cdots N$ interactions have nearly symmetrical bond lengths, but the bond angles are clearly asymmetric. This is possibly due to the movement of some electron density towards N1. In many examples (Koziol *et al.*, 1988), the nitrogen is sp^2 hybridized rather than sp^3 as in the present compound, and therefore the C–N distance is shorter, facilitating the $S \cdots N$ interaction. As in the macrocycle described by Halfpenny & Sloman (2000), the steric restrictions imposed by the C and N atoms being part of the large macrocyclic ring makes such short $S \cdots N$ contacts quite remarkable. They confirm that the electron pairs of the N atoms are directed outside the cavity, which is not favorable for complexation with a metal ion. However, this macrocycle, compared with one having two thiophene groups (Halfpenny & Sloman, 2000), shows greater flexibility in solution, allowing the cavity to accommodate small as well as large metal cations.

The molecules are linked by hydrogen bonds (Table 2). Fig. 2 shows the packing arrangement, giving a chain along the *a* axis.

Experimental

Compound (I) was synthesized using method A described by Chaffin *et al.* (2001). It was dissolved with stirring in a minimum of a 1:1:1 mixture of methanol/diethyl ether/dichloromethane. Slow evaporation at 277 K gave yellow blocks suitable for X-ray crystallographic analysis.

Crystal data

$C_{34}H_{46}N_2O_6S_4$	$V = 842.9(2) \text{ \AA}^3$
$M_r = 706.97$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.393 \text{ Mg m}^{-3}$
$a = 6.8178(9) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.4311(18) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$c = 13.833(2) \text{ \AA}$	$T = 153(2) \text{ K}$
$\alpha = 105.69(2)^\circ$	Block, yellow
$\beta = 92.453(18)^\circ$	$0.30 \times 0.30 \times 0.30 \text{ mm}$
$\gamma = 98.79(2)^\circ$	

Data collection

STOE IPDS diffractometer
 φ scans
 Absorption correction: none
 6702 measured reflections

3075 independent reflections
 2468 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25.9^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.071$
 $S = 0.97$
 3075 reflections
 209 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–C2	1.374 (2)	C9–C10	1.367 (2)
C1–C17 ⁱ	1.494 (2)	C9–O3	1.3727 (18)
C1–S1	1.7245 (14)	C9–C12	1.424 (2)
C2–O1	1.3744 (18)	C10–C13	1.494 (2)
C2–C3	1.416 (2)	C10–S2	1.7251 (15)
C3–C4	1.357 (2)	C11–C12	1.358 (2)
C4–S1	1.7147 (18)	C11–S2	1.7065 (16)
C5–O1	1.4349 (18)	C13–N1	1.4758 (18)
C5–C6	1.499 (2)	C14–N1	1.4710 (19)
C6–O2	1.426 (2)	C14–C15	1.521 (2)
C7–O2	1.4231 (19)	C15–C16	1.518 (2)
C7–C8	1.506 (2)	C17–N1	1.4739 (18)
C8–O3	1.4329 (17)	C17–C1 ⁱ	1.494 (2)
C2–C1–C17 ⁱ	128.46 (13)	C9–C10–S2	109.68 (11)
C2–C1–S1	109.63 (12)	C13–C10–S2	122.34 (10)
C17 ⁱ –C1–S1	121.44 (10)	C12–C11–S2	112.27 (12)
C1–C2–O1	119.10 (15)	C11–C12–C9	111.38 (13)
C1–C2–C3	114.16 (13)	N1–C13–C10	113.45 (13)
O1–C2–C3	126.72 (14)	N1–C14–C15	114.07 (14)
C4–C3–C2	111.80 (14)	C16–C15–C14	113.43 (13)
C3–C4–S1	112.00 (13)	N1–C17–C1 ⁱ	113.40 (12)
O1–C5–C6	107.24 (14)	C14–N1–C17	111.82 (11)
O2–C6–C5	111.60 (12)	C14–N1–C13	107.99 (12)
O2–C7–C8	111.30 (13)	C17–N1–C13	110.93 (10)
O3–C8–C7	107.47 (12)	C2–O1–C5	116.08 (13)
C10–C9–O3	119.54 (13)	C7–O2–C6	115.95 (13)
C10–C9–C12	114.17 (13)	C9–O3–C8	116.48 (12)
O3–C9–C12	126.29 (13)	C4–S1–C1	92.39 (8)
C9–C10–C13	127.96 (13)	C11–S2–C10	92.48 (7)
C9–C10–C13–N1	–108.44 (17)	C3–C2–O1–C5	–12.3 (2)
S2–C10–C13–N1	73.47 (15)	C10–C9–O3–C8	171.75 (13)
C1–C2–O1–C5	168.99 (13)	C12–C9–O3–C8	–8.3 (2)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3–H3A \cdots O2 ⁱⁱ	0.95	2.50	3.142 (2)	125
C13–H13A \cdots O3	0.99	2.58	2.9636 (18)	103

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

H atoms were positioned geometrically and treated as riding atoms, with $C-H = 0.95-0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl groups].

Data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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