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11-Carboxylatomethyl-15-carboxymethyl-11,15-diazonia-3,23-dioxa-28-thiatetracyclo[23.2.1.$0^{4,9}$.$0^{17,22}$]octacosa-4,6,8,17,19,21,25,27-octaene bromide

YIN-HAN ZHANG,[a] SUCHADA CHANTRAPROMMA,[b] S. SHANMUGA SUNDARA RAJ,[c] HOONG-KUN FUN,[c] YU-PENG TIAN,[d] FU-XIN XIE[d] AND ZU-YAO CHEN[a]

[a]*Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China,* [b]*Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand,* [c]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and* [d]*Department of Chemistry, Anhui University, Hefei, Anhui 230039, People's Republic of China. E-mail: suchada@ratree.psu.ac.th*

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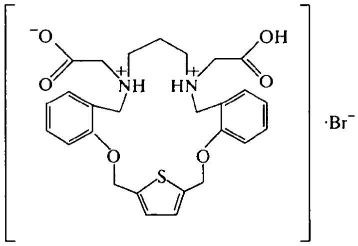
Abstract

The title compound, $C_{27}H_{31}N_2O_6S^+\cdot Br^-$, has crystallographic mirror symmetry. The C—S distance of the thiophene ring is 1.702 (3) Å. The C—H···π interaction influences the crystal packing in addition to N—H···O, O—H···O and C—H···O interactions.

Comment

Selective complexation of macrocyclic ligands with specific metal ions is an important and rapidly expanding area of research (Van Veggel *et al.*, 1994). Zhang *et al.* (1998) and Adam *et al.* (1988) have investigated the complexing properties of macrocyclic ligands with N substituted by acetic acid. The title molecule, (I), is one such macrocyclic ligand and its structure is presented here.



(I)

The mirror-symmetric title compound has half a molecule in the asymmetric unit and the other half related by a mirror plane passing through atoms Br, C14 and S1 with no cavity inside. The results of the room temperature structure determination agree with the values reported for similar compounds. The C—S distance of the thiophene ring [1.702 (3) Å] is comparable with 1.723 (3) Å (Shanmuga Sundara Raj *et al.*, 1999) and slightly longer than 1.69 (1) (Morgant *et al.*, 1996) and 1.694 (4) Å (Youping *et al.*, 1995). The C—O distances of the carbonyl group [C12—O2 = 1.209 (4) and C12—O3 = 1.272 (4) Å] show that it is partially double-bonded and ionized. It is interesting to note that the ligand is zwitterionic, rather than in the 2+ state implied by protonation of N1.

The C2—C3—O1—C4 torsion angle [−170.6 (3)°] shows that the orientation of the phenyl ring is anti-periplanar with respect to the thiophene moiety. In the N—C—C—C—N chain the conformation is *anti–gauche–anti–anti*. The thiophene moiety deviates slightly from the mean plane of the whole molecule [dihedral angle 7.6 (3)°], while the phenyl ring makes a dihedral angle of 26.4 (2)° with the macrocycle. The methyl acetate group is nearly perpendicular to the macrocycle [interplanar angle 82.1 (3)°] and is in a synclinal orientation with respect to the phenyl ring. The thiophene moiety is highly disordered and exists in a planar conformation, with the two conformers in crossed positions. The value of the dihedral angle [61.5 (2)°] between the planar phenyl ring and the methyl acetate group indicates a large folding of the ligand. Analysis of the structure using *PLATON* (Spek, 1990) showed there are no solvent-accessible voids in the structure. The calculation of the least-squares plane shows that the methyl acetate group is planar, with a maximum deviation of −0.015 (3) Å for C11. Atom O1 is coplanar with the phenyl ring [deviation 0.017 (3) Å], but C10 deviates from planarity by −0.139 (3) Å.

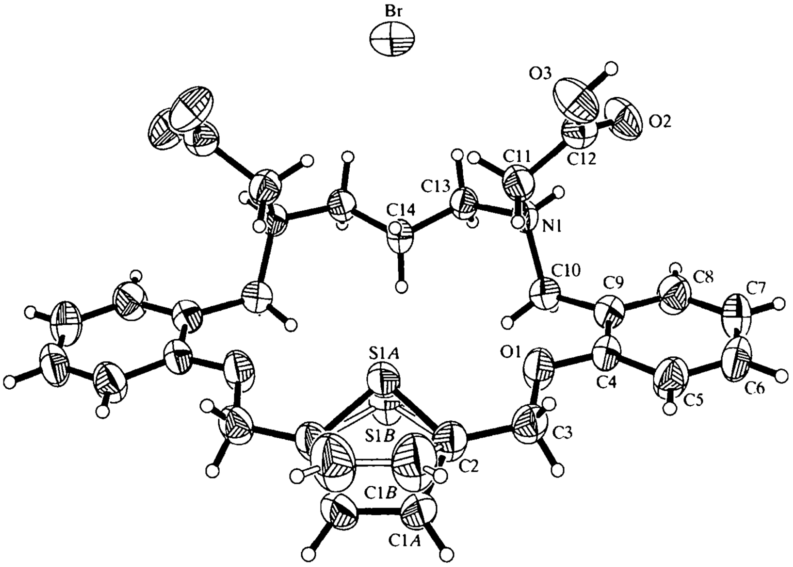


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of arbitrary radius.

The packing of the molecules in (I) is stabilized by intra- and intermolecular N—H···O and C—H···O hydrogen bonding. It is noteworthy that the molecules are connected by O—H···O acid bonds between the acetate groups. The position of the Br atom is fixed inside the cavity formed by three units, through intra- and inter-molecular C—H···Br interactions involving C11 [C11···Br = 3.734 (3) Å, Table 2]. Fig. 2 shows the molecular packing, in which the molecules run parallel to the *c* axis as infinite chains are formed. The chain looks like an elongated spring.

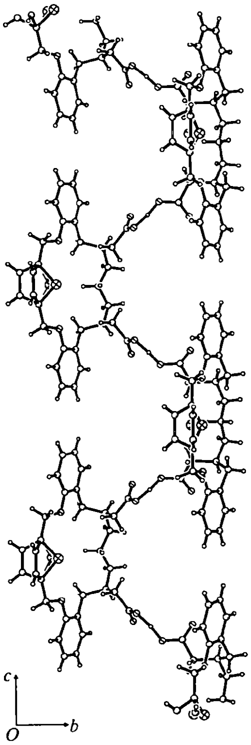


Fig. 2. The packing of the molecules in (I) viewed down the *a* axis.

Experimental

The preparation of the parent macrocycle, 1,5-diaza-3,4:12,13-dibenzo-5,11-dioxa-2′,5′-thiophenecyclononadecane, was reported by Adam *et al.* (1983). A dry methanol solution of sodium hydroxide (0.05 mol in 50 ml) was added to a dry methanol solution of bromoacetic acid (7 g, 0.05 mol in 50 ml) below 283 K. This mixture was added stepwise to a mixture of the parent macrocycle (0.08 mol) and powdered anhydrous sodium carbonate (0.1 mol) in methanol (150 ml) over about 1 h, and the resulting mixture was refluxed with stirring for 24 h. The mixture was then cooled and the white precipitate of sodium hydrogen carbonate was filtered off. After nearly complete evaporation of the solvent, distilled water (200 ml) was added to the residue, the white precipitate of unreacted parent macrocycle was filtered off and the solution was acidified to pH 2–3 with hydrobromic acid to obtain the product, (I), as a white solid (yield 62.5%).

Crystal data

$C_{27}H_{31}N_2O_6S^+\cdot Br^-$
$M_r = 591.51$
Orthorhombic
Pbcm
$a = 10.9776\,(1)$ Å
$b = 14.0734\,(2)$ Å
$c = 17.3262\,(2)$ Å
$V = 2676.76\,(5)$ Å^3
$Z = 4$
$D_x = 1.468$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8033 reflections
$\theta = 1.17$–$38.61°$
$\mu = 1.658$ mm^{-1}
$T = 293\,(2)$ K
Slab
0.40 × 0.36 × 0.16 mm
White

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical using *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.557$, $T_{\max} = 0.777$
18 432 measured reflections
3180 independent reflections
2460 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 27.49°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 20$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.182$
$S = 1.077$
3180 reflections
190 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1009P)^2 + 2.4231P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1*A*—C2	1.702 (3)	O1—C3	1.436 (4)
O1—C4	1.366 (4)		
C11—N1—C10	114.6 (3)	O2—C12—O3	126.9 (4)
C11—N1—C13	112.3 (2)	O2—C12—C11	122.0 (3)
C10—N1—C13	111.5 (2)	O3—C12—C11	111.1 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O2	0.90	2.22	2.753 (4)	118
C10—H10*A*···O1	0.97	2.31	2.758 (4)	107
C11—H11*B*···Br	0.97	2.87	3.734 (3)	149
O3—H3*C*···O3$^{\rm i}$	1.22	1.22	2.423 (4)	163
N1—H1N1···O2$^{\rm ii}$	0.90	2.10	2.874 (4)	143
C8—H8*A*···O2$^{\rm ii}$	0.93	2.59	3.392 (5)	145
C11—H11*B*···Br	0.97	2.87	3.734 (3)	149

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

The thiophene ring is highly disordered over two orientations: atoms S1 and C1 were refined with occupancies of 72 and 28%, respectively.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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N,*N*′-Bis(picolinoyl)hydrazine

Sichang Shao,[a]† Dunru Zhu,[a] You Song,[a] Xiao Zeng You,[a] S. Shanmuga Sundara Raj[b] and Hoong-Kun Fun[b]

[a]*Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

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Abstract

The X-ray structure determination of the title compound, *N*,*N*′-bis(2-pyridinecarbonyl)hydrazine, $C_{12}H_{10}N_4O_2$,

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† Visiting Scholar from: Fuyang Normal College, 236032 Anhui, People's Republic of China.