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2,9-Bis(methoxymethyl)-1,3,8,10-tetrathiacyclotetradecane

Zeynep Gültekin,[a] Hacer Bayrak,[a] Wolfgang Frey[b] and Tuncer Hökelek[c]*

[a]Zonguldak Karaelmas University, Department of Chemistry, 067100 Zonguldak, Turkey, [b]Universitat Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany, and [c]Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey

Correspondence e-mail:
merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.050
wR factor = 0.143
Data-to-parameter ratio = 16.3

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

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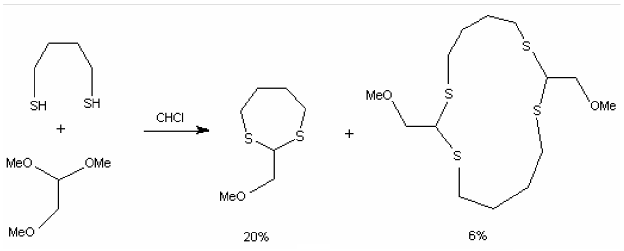
The title compound, $C_{14}H_{28}O_2S_4$, possesses a crystallographically imposed inversion centre and has two methine C atoms linked to methoxymethyl functional groups. It is in the exodentate conformation, with the four S atoms lying on the edges of the 'rectangular' macrocycle. The lone pairs of electrons on the S atoms point outwards from the macrocyclic cavity and the S atoms are bridged alternately by one-carbon and four-carbon moieties.

Comment

Macrocycles which have been the subject of structural studies include nitrogen and oxygen donor systems envisaged as models for corrin and/or porphyrin systems, ion-transfer agents and natural antibiotics (Nave & Truter, 1974; Dunitz & Seiler, 1974; Dobler & Phizackerley, 1974; Dobler *et al.*, 1974; Hökelek *et al.*, 1993, 1999, 2002, 2003; Bilge *et al.*, 2002; Hayvalı *et al.*, 2003).

Macrocyclic thioether ligands act as capping ligands, favouring both the blocking of transition metal coordination sites and the formation of discrete metal complexes in coordination chemistry (Blake & Schröder, 1990; Blake *et al.*, 2000; Grant *et al.*, 2000; Pillinger *et al.*, 2001; Nunes *et al.*, 2003). In the free ligands, all the sulfur electron lone pairs are in the exodentate conformation, which, in view of their bridging potential, is an arrangement perfectly suited for the generation of coordination polymers.

The synthesis and properties of polythiaether macrocycles and their transition metal complexes have further extended the scope of macrocyclic chemistry (Rosen & Busch, 1969; Ochrymowycz *et al.*, 1974). Polyether macrocycles or thiacrowns, as they are commonly called, constitute an extensive family of large-ring heterocycles. Strained ring thioethers have been used for the preparation of thiacrown ethers such as thietane and thiirane reagents (Adams & Falloon, 1994, 1995; Adams *et al.*, 1997).



(I)

We have developed a new thiacrown ether, (I), which can be readily obtained in one step using 1,4-butanedithiol and methyl acetaldehyde dimethyl acetal. The title compound, (I),

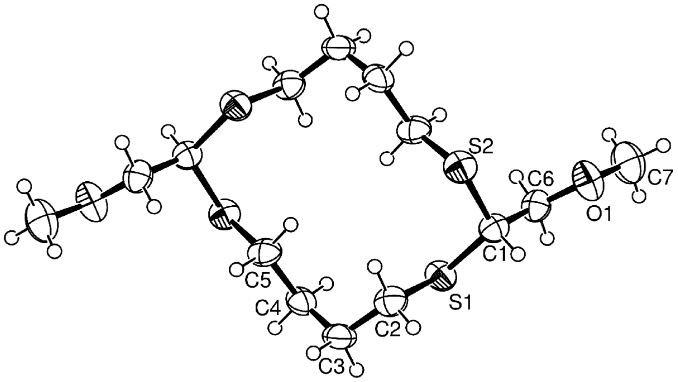


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

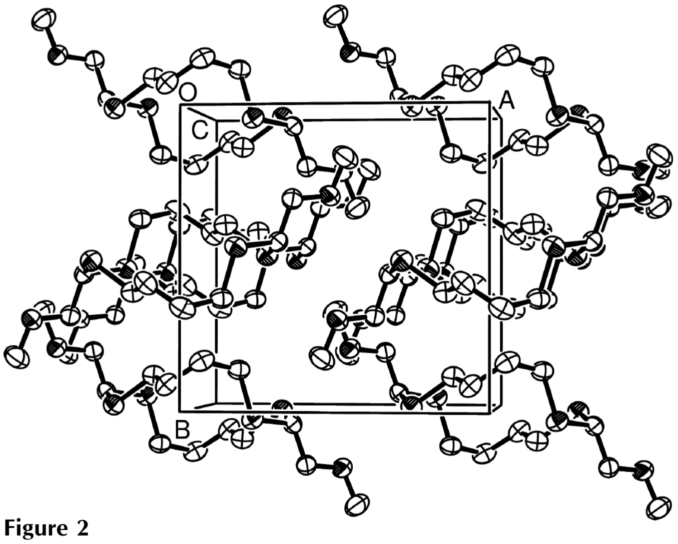


Figure 2
A packing diagram for (I). H atoms have been omitted for clarity.

also has useful functional groups in the 2- and 9-positions, allowing easy transformation into the alkene, using methods reported by Aggarwal *et al.* (1998). It may also be a useful ligand for coordination chemistry.

In the title compound, (I), each of the two methine C atoms is linked to a methoxymethyl functional group. Compound (I) is in the exodentate conformation, with the lone pair electrons of the four S atoms pointing outwards from the edges of the approximately rectangular macrocycle. The S atoms are bridged alternately by one-carbon and four-carbon moieties (Fig. 1) and the resulting adduct has an inversion centre at the centre of the ring.

The macrocyclic conformation differs from that seen in the free ligand 1,4,8,11-tetrathiacyclotetradecane, (II) (DeSimone & Glick, 1976), which has the [3434] 'rectangular' diamond lattice conformation (Dale, 1973). Although the title compound, (I), also has a [3434] conformation, it differs from (II) by having the S atoms lying along the edges rather than at the corners of the macrocycle. In the exodentate conformation, the optimum values of the torsion angles in the macrocyclic ring must be 180° (*anti*) or 60° (*gauche*) and, in (I), eight are *gauche* and six *anti* (Table 1).

The C—S distances average 1.813 (3) Å, similar to those found in (II) [average 1.809 (3) Å] (DeSimone & Glick, 1976). The C—C distances in the macrocyclic ring average 1.518 (4) Å, somewhat shorter than the expected value of 1.54 Å for a C—C single bond. The C—S—C angles average 102.23 (13)°, less than the tetrahedral angle of 109.5°, as expected.

The ligand cavity plays an important role in metal-ion selectivity. The intramolecular $C1\cdots C1^{i}$ [7.105 (3) Å], $C3\cdots C3^{i}$ [6.475 (3) Å], $C5\cdots C5^{i}$ [4.325 (4) Å], $S1\cdots S1^{i}$ [6.006 (3) Å] and $S2\cdots S2^{i}$ [6.072 (4) Å] distances give an indication of the cavity size in this 14-membered macrocyclic ring [symmetry code: (i) $-x, -y, 1-z$]. The macrocyclic compound is involved in close intermolecular contacts: $C6-H6A$ = 0.97 Å, $H6A\cdots O1^{ii}$ = 2.79 Å and $C6-H6A\cdots O1^{ii}$ 167°; $C1-H1$ = 0.98 Å, $H1\cdots O1^{iii}$ = 2.49 Å and $C1-H1\cdots O1^{iii}$ 144°; symmetry codes: (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, -y, 1-z$]. These may play a role in the macrocyclic inner cavity size contraction.

As can be seen from the packing diagram (Fig. 2), the macrocyclic molecules are elongated approximately parallel to the *b* axis and stacked along the *c* axis. In addition to the intermolecular close contacts, dipole–dipole and van der Waals interactions also play a part in the molecular packing.

Experimental

1,4-Butanedithiol (10.7 ml, 89.4 mmol) and concentrated hydrochloric acid (8.4 ml) were cooled to 273 K and methyl acetaldehyde dimethyl acetal (10.48 ml, 81.3 mmol) was added over 20 min, using a syringe. After a further 30 min, the ice bath was removed and the reaction mixture was stirred for 3 h at room temperature. The resulting two-phase mixture was partitioned between dichloromethane (35 ml) and water (35 ml). The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 35 ml). The combined organic layers were washed with saturated $NaHCO_3$ (40 ml) and brine (40 ml), and the organic layer was then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the viscous and colourless residue was subjected to flash chromatography, eluting with 10:90 acetone:petroleum ether to afford the title compound as a white solid (yield 2.0 g, 6%; m.p. 359–360 K) and 2-methoxymethyl-1,3-dithiepane as an oil. Recrystallization from petroleum ether gave colourless crystals.

Crystal data

$C_{14}H_{28}O_2S_4$
M_r = 356.64
Monoclinic, $P2_1/c$
a = 10.5512 (10) Å
b = 10.4538 (12) Å
c = 8.2152 (10) Å
β = 91.061 (10)°
V = 905.98 (17) Å^3
Z = 2
D_x = 1.307 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12–18°
μ = 0.52 mm^{-1}
T = 293 (2) K
Plate, colourless
0.40 × 0.20 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
Non-profiled ω scans
Absorption correction: none
1619 measured reflections
1497 independent reflections
1262 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 25.2°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 9$
2 standard reflections every 50 reflections
intensity decay: 1%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.143$
$S = 1.02$
1497 reflections
92 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1005P)^2 + 0.1736P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.13 (2)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.805 (3)	C3—C2	1.517 (4)
S1—C1	1.821 (3)	C3—C4	1.525 (4)
S2—C5^{i}	1.812 (3)	C6—C1	1.524 (4)
S2—C1	1.815 (3)	C4—C5	1.511 (4)
O1—C6	1.406 (3)	C5—S2^{i}	1.812 (3)
O1—C7	1.407 (4)		
C2—S1—C1	101.97 (13)	C5—C4—C3	113.1 (2)
C5^{i}—S2—C1	102.26 (12)	C6—C1—S2	113.7 (2)
C6—O1—C7	111.5 (2)	C6—C1—S1	105.64 (19)
C2—C3—C4	115.6 (2)	S2—C1—S1	115.24 (13)
C3—C2—S1	109.8 (2)	C4—C5—S2^{i}	109.8 (2)
O1—C6—C1	109.0 (2)		
C4—C3—C2—S1	−62.0 (3)	C5^{i}—S2—C1—C6	66.7 (2)
C1—S1—C2—C3	173.99 (19)	C5^{i}—S2—C1—S1	−55.40 (18)
C7—O1—C6—C1	177.4 (3)	C2—S1—C1—C6	179.82 (18)
C2—C3—C4—C5	−66.5 (3)	C2—S1—C1—S2	−53.85 (18)
O1—C6—C1—S2	67.4 (2)	C3—C4—C5—S2^{i}	178.50 (19)
O1—C6—C1—S1	−165.31 (18)		

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

H atoms were positioned geometrically at distances of 0.98 (CH), 0.97 (CH_2) and 0.96 Å (CH_3) from the parent C atoms; a riding model was used during the refinement process. The $U_{\rm iso}$ values were constrained to be 1.2 (1.5 for methyl group) times $U_{\rm eq}$ of the carrier atom.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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