C(48)	0.8030 (8)	0.6294 (5)	0.3745 (3)	0.057 (1)
N(4″)	1.3766 (5)	0.3270 (3)	0.4772 (2)	0.040 (1)
C(5″)	1.5123 (7)	0.4161 (4)	0.5101 (2)	0.043 (1)
O(5″)	1.4869 (5)	0.5409 (3)	0.5057 (2)	0.058 (1)
C(6″)	1.6977 (7)	0.3570 (5)	0.5541 (2)	0.055 (1)
Cl(1)	1.7879 (2)	0.5720†	0.7659 (1)	0.084 (1)
Cl(2)	1.5131 (2)	0.3519 (2)	0.7841 (1)	0.098 (1)
Cl(3)	1.9438 (3)	0.3019 (2)	0.7859 (2)	0.130 (1)
C(1L)	1.7593 (8)	0.4150 (5)	0.8084 (3)	0.065 (2)

† Coordinate fixed to define origin.

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(2)	1.399 (4)	N(1)—C(6)	1.375 (5)
N(1)—C(1′)	1.457 (4)	C(2)—O(2)	1.233 (4)
C(2)—N(3)	1.348 (4)	N(3)—C(4)	1.308 (5)
C(4)—C(5)	1.411 (5)	C(4)—O(4)	1.333 (4)
C(5)—C(6)	1.341 (5)	C(1′)—O(4′)	1.421 (5)
C(1′)—C(2′)	1.512 (5)	O(4′)—C(4′)	1.419 (4)
C(2′)—C(3′)	1.517 (5)	C(3′)—O(3′)	1.430 (6)
C(3′)—C(4′)	1.520 (6)	C(4′)—C(5′)	1.509 (5)
C(5′)—O(5′)	1.413 (6)	O(4)—C(41)	1.418 (4)
C(41)—C(42)	1.391 (6)	C(41)—C(46)	1.378 (5)
C(42)—C(47)	1.506 (6)	C(42)—C(43)	1.390 (5)
C(43)—C(44)	1.377 (5)	C(44)—C(45)	1.400 (5)
C(44)—N(4″)	1.409 (4)	C(45)—C(46)	1.390 (5)
C(46)—C(48)	1.513 (6)	N(4″)—C(5″)	1.339 (5)
C(5″)—O(5″)	1.239 (4)	C(5″)—C(6″)	1.492 (6)
Cl(1)—C(1L)	1.743 (5)	Cl(2)—C(1L)	1.743 (5)
Cl(3)—C(1L)	1.732 (6)		

C(2)—N(1)—C(6)	120.5 (3)	C(2)—N(1)—C(1′)	117.7 (3)
C(6)—N(1)—C(1′)	121.8 (3)	N(1)—C(2)—O(2)	119.0 (3)
N(1)—C(2)—N(3)	118.5 (3)	O(2)—C(2)—N(3)	122.4 (3)
C(2)—N(3)—C(4)	119.4 (3)	N(3)—C(4)—C(5)	124.6 (3)
N(3)—C(4)—O(4)	119.4 (3)	C(5)—C(4)—O(4)	115.9 (3)
C(4)—C(5)—C(6)	115.9 (3)	N(1)—C(6)—C(5)	120.7 (3)
N(1)—C(1′)—O(4′)	108.6 (3)	N(1)—C(1′)—C(2′)	115.7 (3)
O(4′)—C(1′)—C(2′)	104.3 (3)	C(1′)—O(4′)—C(4′)	108.3 (3)
C(1′)—C(2′)—C(3′)	100.9 (3)	C(2′)—C(3′)—O(3′)	111.1 (3)
C(2′)—C(3′)—C(4′)	102.8 (3)	O(3′)—C(3′)—C(4′)	106.9 (4)
O(4′)—C(4′)—C(3′)	107.4 (3)	O(4′)—C(4′)—C(5′)	109.0 (3)
C(3′)—C(4′)—C(5′)	114.3 (3)	C(4′)—C(5′)—O(5′)	112.5 (4)
C(4)—O(4)—C(41)	118.5 (3)	O(4)—C(41)—C(42)	117.1 (3)
O(4)—C(41)—C(46)	119.5 (3)	C(42)—C(41)—C(46)	123.3 (3)
C(41)—C(42)—C(47)	121.1 (4)	C(41)—C(42)—C(43)	116.9 (3)
C(47)—C(42)—C(43)	122.0 (4)	C(42)—C(43)—C(44)	121.9 (3)
C(43)—C(44)—C(45)	119.4 (3)	C(43)—C(44)—N(4″)	117.3 (3)
C(45)—C(44)—N(4″)	123.2 (3)	C(44)—C(45)—C(46)	120.3 (3)
C(41)—C(46)—C(45)	118.2 (3)	C(41)—C(46)—C(48)	121.7 (3)
C(45)—C(46)—C(48)	120.1 (3)	C(44)—N(4″)—C(5″)	130.5 (3)
N(4″)—C(5″)—O(5″)	122.8 (4)	N(4″)—C(5″)—C(6″)	116.1 (3)
O(5″)—C(5″)—C(6″)	121.1 (4)	Cl(1)—C(1L)—Cl(2)	110.6 (3)
Cl(1)—C(1L)—Cl(3)	110.4 (3)	Cl(2)—C(1L)—Cl(3)	111.8 (3)

Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was carried out by full-matrix least-squares methods with *XLS* (Sheldrick, 1987). All H atoms were located by a difference synthesis and positioned with fixed individual displacement parameters [$U(H) = 1.5 \times U_{eq}(C_{methyl})$ or $U(H) = 1.2 \times U_{eq}(C, N, O)$] using a riding model with C—H = 0.96, N—H 0.90 and O—H 0.85 Å. An empirical isotropic extinction correction was applied for which $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-0.25}$, where χ refined to a value of 0.012 (2). The absolute configuration was determined by η-refinement (Rogers, 1981) starting from both configurations [$\eta = 0.94$ (4) for the correct structure].

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6-Oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene

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Abstract

The title molecule, $C_{12}H_{16}OS_2$, is partially disordered with the O and H atoms of the —CH_2—O—CH_2— group occupying two positions. The molecule assumes C_2 symmetry and the twofold axis is located midway through the triene group and across the two partially occupied O-atom positions.

Comment

Thiocrown macrocycles have come into prominence because of their ability to stabilize unusual transition metal oxidation states (Blake & Schröder, 1990). In addition, it has been demonstrated that some of these molecules have the capability to act as neutral carriers for silver(I)-selective membrane electrodes (Casabó, Mestres, Escriche, Teixidor & Perez-Jimenez, 1991). We have studied the fluxionality of xylene-based thiocrown conformations with the aim of improving selectivity towards silver as opposed to other thiophilic metal ions. These studies are based on the interpretation of ^1H NMR solution-coupling information and molecular dynamics (MD) simulations (Lockhart et al., 1992). Crystal structures are used as input parameters in theoretical MD calculations as they represent the low-energy conformations existing in fluid phases (Murray-Rust, Bürgi & Dunitz, 1975). In this context we present here the crystal structure of the thiocrown macrocycle 6-oxa-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene (I).

(I)
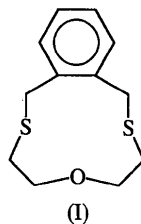
The molecule is partially disordered with the O(1) atom and the H atoms bonded to C(6) occupying two positions. The disorder assumes C_2 symmetry and the twofold axis is located midway through the atom pairs C(1)–C(1^i) and C(3)–C(3^i) [symmetry code: (i) $1-x$, y, $\frac{3}{2}-z$], and across the two partially occupied O(1) atom positions. The disorder is due to the flexible nature of the heterocyclic chain. On the other hand, if the O(1) atom were exactly on the C_2 axis this could cause some strain in the chain. The S atoms and the disordered O atom have an endodentate conformation, but owing to the molecular symmetry, the S atoms occupy different sides of the approximately planar 1,2-dimethylbenzene moiety. Thus, the observed geometry is not suitable for tridentate OS_2 coordination of a metal ion. Comparison of the conformations of the title ligand and the related trithia compounds, the free ligand 2,5,8-trithia[9]-o-benzenophane (oS$_3$) (Lockhart et al., 1992) and the complexes [Hg(NO$_3$)(oS$_3$)(PPh$_3$)]$^+$ (Kivekäs et al., 1994), [CuCl(oS$_3$)] and [Ni(oS$_3$)$_2$]$^{2+}$ (Escriche et al., 1993), reveals considerable differences. The molecular symmetry of the oS$_3$ ligands is lower (C_1) and the conformations are different from that in the title compound. In the metal complexes, each oS$_3$ ligand is tridentately coordinated to the metal and the S atoms have an overall endodentate conformation. In the free oS$_3$ ligand the S atoms have an exodentate

conformation which is not suitable for tridentate S$_3$ coordination (Lockhart et al., 1992). These differences can also be seen by comparing the C(1^i)—C(1)—C(4)—S(1) torsion angles in the title compound and the corresponding angles in the free oS$_3$ ligand and the Hg complex. The torsion angle values are: 76.5 (3)° in the title compound, -138.7 (3) and 128.4 (4)° in oS$_3$, and -86 (2) and 104 (1)° in the Hg compound. Thus, substitution of the O atom in the title compound by S considerably changes the geometry of the molecule and lowers the molecular symmetry from C_2 to C_1 in the solid state. Moreover, complexation of oS$_3$ with Hg^{2+} further changes its conformation. These differences are further confirmation of the flexibility of this type of macrocyclic molecule.
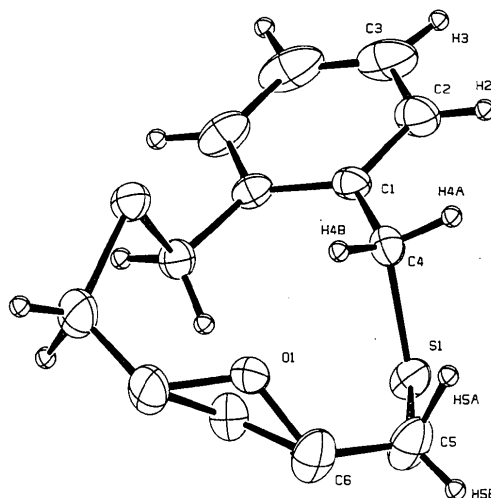

Fig. 1. ORTEPII (Johnson, 1976) plot of $C_{12}H_{16}OS_2$. The disordered H atoms bonded to C(6) have been omitted. Displacement ellipsoids are shown at the 50% probability level, except for H atoms which are given arbitrary radii.

Experimental

The title compound was synthesized and crystallized as reported in the literature (Casabó, Mestres, Escriche, Teixidor & Perez-Jimenez, 1991), but the oily material was extracted with toluene instead of benzene [yield 2.1 g (43%)].

Crystal data

$C_{12}H_{16}OS_2$	Mo $K\alpha$ radiation
$M_r = 240.38$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 11.069$ (1) Å	$\theta = 18.2–21.1°$
$b = 11.208$ (1) Å	$\mu = 0.396$ mm^{-1}
$c = 9.915$ (1) Å	$T = 296$ K
$\beta = 101.396$ (9)°	Prism
$V = 1205.8$ (2) Å^3	$0.35 \times 0.30 \times 0.20$ mm
$Z = 4$	Colourless
$D_x = 1.324$ Mg m^{-3}	

Data collection

Rigaku AFC-5S diffractometer	$\theta_{max} = 25°$
ω–2θ scans	$h = 0 \rightarrow 13$
Absorption correction:	$k = 0 \rightarrow 13$
empirical, ψ-scan	$l = -11 \rightarrow 11$
$T_{min} = 0.95$, $T_{max} = 1.00$	3 standard reflections
1185 measured reflections	monitored every 150
1121 independent reflections	reflections
895 observed reflections	intensity variation: decline
$[I > 2\sigma(I)]$	of -1.20%, linear
$R_{int} = 0.010$	correction applied

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.033$
$R = 0.044$	$\Delta\rho_{max} = 0.2$ e Å^{-3}
$wR = 0.055$	$\Delta\rho_{min} = -0.3$ e Å^{-3}
$S = 2.23$	Atomic scattering factors
895 reflections	from *Xtal*3.0 (Hall &
89 parameters	Stewart, 1990)
$w = 1/\sigma^2(F)$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	0.29308 (6)	0.52931 (6)	0.68847 (8)	0.0487 (3)
O(1)†	0.4890 (5)	0.3466 (3)	0.7885 (4)	0.051 (2)
C(1)	0.4610 (2)	0.7084 (2)	0.6846 (3)	0.0423 (9)
C(2)	0.4254 (3)	0.8178 (3)	0.6224 (4)	0.064 (1)
C(3)	0.4636 (3)	0.9239 (3)	0.6856 (5)	0.087 (2)
C(4)	0.4161 (3)	0.5942 (3)	0.6139 (3)	0.045 (1)
C(5)	0.2946 (3)	0.3770 (3)	0.6275 (4)	0.071 (1)
C(6)	0.3968 (3)	0.3017 (3)	0.6893 (4)	0.071 (1)

† Site occupation 0.5.

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(4)	1.825 (3)	C(1)—C(2)	1.393 (4)
S(1)—C(5)	1.812 (4)	C(1)—C(4)	1.497 (4)
O(1)—C(6)	1.366 (5)	C(2)—C(3)	1.371 (5)
O(1)—C(6^i)	1.337 (6)	C(3)—C(3^i)	1.368 (7)
C(1)—C(1^i)	1.409 (4)	C(5)—C(6)	1.447 (5)
C(4)—S(1)—C(5)	100.6 (2)	C(2)—C(3)—C(3^i)	119.9 (3)
C(6)—O(1)—C(6^i)	121.8 (4)	S(1)—C(4)—C(1)	110.9 (2)
C(2)—C(1)—C(4)	120.4 (3)	S(1)—C(5)—C(6)	117.8 (2)
C(2)—C(1)—C(1^i)	118.4 (3)	O(1)—C(6)—C(5)	120.0 (3)
C(4)—C(1)—C(1^i)	121.2 (2)	C(5)—C(6)—O(1^i)	119.0 (3)
C(1)—C(2)—C(3)	121.7 (3)		
C(5)—S(1)—C(4)—C(1)	-161.8 (2)	C(1^i)—C(1)—C(4)—S(1)	76.5 (3)
C(4)—S(1)—C(5)—C(6)	72.2 (3)	C(1)—C(2)—C(3)—C(3^i)	-1.4 (7)
C(6^i)—O(1)—C(6)—C(5)	-153.7 (4)	S(1)—C(5)—C(6)—O(1)	-1.0 (6)
C(4)—C(1)—C(2)—C(3)	179.0 (4)	S(1)—C(5)—C(6)—O(1^i)	-43.1 (5)
C(1^i)—C(1)—C(2)—C(3)	-0.5 (5)	C(5)—C(6)—O(1)—C(6^i)	-153.7 (4)
C(2)—C(1)—C(4)—S(1)	-103.0 (3)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed by full-matrix least-squares methods, non-H atoms with anisotropic displacement parameters and H atoms either with isotropic displacement parameters [H(2), H(3), H(4A) and H(4B)] or included in the calculations at fixed positions (C—H = 0.95 Å). The refinements were carried out with *Xtal*3.0 (Hall & Stewart, 1990). The figure was drawn using *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethyl 2,2'-[1,3-Phenylenebis(methylthio)]-dibenzoate

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Abstract

The title molecule, $C_{26}H_{26}O_4S_2$, assumes C_2 symmetry with two C atoms and two H atoms of the cen-