Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

5,8,11-Trioxa-2,14-dithiabicyclo[13.4.1]icosa-1(19),15,17-trien-20-one

Kanji Kubo *et al.*

Electronic paper
This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

5,8,11-Trioxa-2,14-dithiabicyclo[13.4.1]icosa-1(19),15,17-trien-20-one

Kanji Kubo,* Akira Mori, Nobuo Kato and Hitoshi Takeshita

Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
Correspondence e-mail: kubo-k@cm.kyushu-u.ac.jp

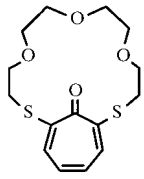
Received 19 June 2000
Accepted 13 July 2000

Data validation number: IUC0000193

The title compound, $C_{15}H_{20}O_4S_2$, crystallizes in a chiral space group although it contains mirror symmetry. The tropone ring is inclined at an angle of 50.3 (1)° to the crown ether ring. The planarity of the tropone ring system itself is diminished by as much as 20.8 (4)°.

Comment

Mercurophilic dithiocrown derivatives having a troponoid pendant (Takeshita *et al.*, 1993; Mori *et al.*, 1996, 1997; Kubo *et al.*, 1998, 2000) were recently prepared since these molecules are excellent carriers of the Hg^{II} ion, which is one of the most critical heavy metal ions from an environmental viewpoint (Bacon & Kirch, 1985, 1987; Izatt *et al.*, 1985*a*,*b*, 1986; Parham & Shamsipur, 1994). Based on their reversible complexation behaviours with Hg^{II} salts, particularly noteworthy is the exclusive and selective transport of the Hg^{II} ion among various metal ions through a liquid membrane. As a matter of efficiency in the transport of the Hg^{II} ion, dithiocrown derivatives condensed with the tropone system showed a dependence on the cavity size of the crown ethers (Mori *et al.*, 1996). This was confirmed by X-ray diffraction studies (Kubo *et al.*, 1995, 1996, 2000; Kato *et al.*, 1995; Mori *et al.*, 1998). In the Hg^{II} salt complex of 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one, which is an excellent carrier of Hg^{II} ion through a liquid membrane, the Hg^{II} ion is at the centre of a dithiacrown ring to form a normal penetrated complex. The title compound, 5,8,11-trioxa-2,14-dithiabicyclo[13.4.1]icosa-1(19),15,17-trien-20-one, (I), formed a (I)–2.5$HgCl_2$–H_2O complex. The Hg^{II} atom in the complexation was not in the cavity of the crown system; a Hg^{II} atom was coordinated by ethereal O atom to form a tetrahedral coordination and the other Hg^{II} atoms are coordinated by both the tropone carbonyl O atom and the thioether sulfur atom to form a side-on complex. In order to reveal the detailed structure of troponoid dithiocrown derivatives and their complexes, (I) has been investigated by an X-ray crystallographic analysis.



(I)

The title compound crystallizes in a chiral space group although it contains mirror symmetry. The tropone ring defined by atoms O1 and C1–C7 makes an angle of 50.3 (1)° with the crown ether ring defined by atoms S1, O2–O4 and S2. The conformation of the ethereal moiety is S(*g*)C(*g*)C(*t*)O(*t*)C(*g*)C(*t*)O(*t*)C(*g*)C(*t*)O(*t*)C(*g*)C(*g*)S, where *t* and *g* denote *trans* and *gauche* forms, respectively. The conformation of all CH_2—O bonds was *trans* and distinct from that [S(*g*)C(*g*)C(*t*)O(*t*)C(*g*)C(*g*)O(*t*)C(*g*)C(*t*)O(*g*)C(*g*)C(*g*)S] of (I)–2.5$HgCl_2$–H_2O (Kubo *et al.*, 2000). On the other hand, the angle between the least-squares planes C1/C2/C7 and C2/C3/C6/C7 is 20.8 (4)°. The corresponding angle of (I) is smaller than that (33.8°) of 5-oxa-2,8-dithiabicyclo[7.4.1]-tetradeca-9,11,13-trien-14-one (Mori *et al.*, 1998) and similar to that (20.4°) of the $HgCl_2$ complex of 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricosa-1(22),18,20-trien-23-one (Kubo *et al.*, 1996). This means that the larger ethereal ring of the crown ethers leads to a smaller deviation from planarity of the seven-membered ring of (I). The angle (20.8°) of (I) is larger than that (7.5°) of (I)–2.5$HgCl_2$–H_2O, suggesting that the complexation with Hg^{II} decreases the deviation from planarity of the seven-membered ring. Interestingly, all tropone C—O, C—C and C—S bond lengths of (I) are similar to those of (I)–2.5$HgCl_2$–H_2O (Kubo *et al.*, 2000).

Experimental

The title compound, (I), was obtained by condensation from NaH-mediated 3,6,9-trioxa-1,11-undecanedithiol and 2,7-dibromotropone (Takeshita *et al.*, 1993). Single crystals of (I) were obtained by crystallization from $CHCl_3$.

Crystal data

$C_{15}H_{20}O_4S_2$
M_r = 328.43
Orthorhombic, $P2_12_12_1$
a = 9.682 (5) Å
b = 18.654 (5) Å
c = 8.977 (5) Å
V = 1621.3 (13) Å^3
Z = 4
D_x = 1.346 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.6–18.3°
μ = 0.340 mm^{-1}
T = 296 (2) K
Prism, yellow
0.40 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.879, T_{max} = 0.903
2032 measured reflections
2032 independent reflections
1420 reflections with $I > 2\sigma(I)$
θ_{max} = 26.97°
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 1.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0400P)^2 + 0.4494P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.102$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.020$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
2032 reflections	Absolute structure: Flack (1983)
190 parameters	Flack parameter = 0.00 (17)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C7	1.769 (4)	C2—C3	1.365 (5)
S2—C2	1.760 (4)	C3—C4	1.401 (5)
O1—C1	1.236 (4)	C4—C5	1.348 (6)
C1—C7	1.459 (5)	C5—C6	1.394 (6)
C1—C2	1.467 (5)	C6—C7	1.371 (5)
C7—S1—C8	106.6 (2)	C2—S2—C15	104.76 (19)
C7—S1—C8—C9	78.8 (4)	C11—O3—C12—C13	−174.4 (4)
C10—O2—C9—C8	−176.9 (4)	C14—O4—C13—C12	177.1 (4)
S1—C8—C9—O2	−66.9 (5)	O3—C12—C13—O4	−91.7 (6)
C9—O2—C10—C11	−175.7 (4)	C13—O4—C14—C15	−175.8 (4)
C12—O3—C11—C10	−174.8 (5)	O4—C14—C15—S2	66.2 (4)
O2—C10—C11—O3	73.0 (6)	C2—S2—C15—C14	−75.7 (3)

All H atoms were calculated at ideal positions and constrained to ride on their parent atoms. Isotropic displacement parameters of H atoms were fixed at $1.2U_{eq}$ of the parent atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bacon, E. & Kirch, M. (1985). *J. Membr. Sci.* **24**, 185–199.

Bacon, E. & Kirch, M. (1987). *J. Membr. Sci.* **32**, 159–173.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Izatt, R. M., Bruening, R. L., Clark, G. A., Lamb, J. D. & Christensen, J. J. (1985*a*). *J. Membr. Sci.* **26**, 77–86.

Izatt, R. M., Clark, G. A. & Christensen, J. J. (1985*b*). *J. Membr. Sci.* **24**, 1–5.

Izatt, R. M., Jones, M. B., Lamb, J. D., Bradshaw, J. S. & Christensen, J. J. (1986). *J. Membr. Sci.* **26**, 241–250.

Kato, N., Kubo, K., Mori, A. & Takeshita, H. (1995). *Heterocycles*, **41**, 1901–1904.

Kubo, K., Kato, N., Mori, A. & Takeshita, H. (1995). *Chem. Lett.* pp. 629–630.

Kubo, K., Kato, N., Mori, A. & Takeshita, H. (2000). *Heterocycles*, **53**, 535–538.

Kubo, K., Mori, A., Kato, N. & Takeshita, H. (1996). *Acta Cryst.* C**52**, 1656–1658.

Kubo, K., Mori, A., Kato, N. & Takeshita, H. (1998). *Heterocycles*, **49**, 385–392.

Mori, A., Kubo, K., Kato, N., Takeshita, H., Shiono, M. & Achiwa, N. (1998). *Heterocycles*, **47**, 149–152.

Mori, A., Kubo, K. & Takeshita, H. (1996). *Coord. Chem. Rev.* **148**, 71–96.

Mori, A., Kubo, K. & Takeshita, H. (1997). *Heterocycles*, **46**, 509–516.

North, A. T. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Parham, H. & Shamsipur, M. (1994). *J. Membr. Sci.* **86**, 29–35.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Takeshita, H., Yin, B. Z., Kubo, K. & Mori, A. (1993). *Bull. Chem. Soc. Jpn*, **66**, 3451–3455.