

20-Dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]-tricoso-1(23),18,21-triene and its mercury(II) dichloride complex

Kanji Kubo,* Nobuo Kato, Akira Mori* 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

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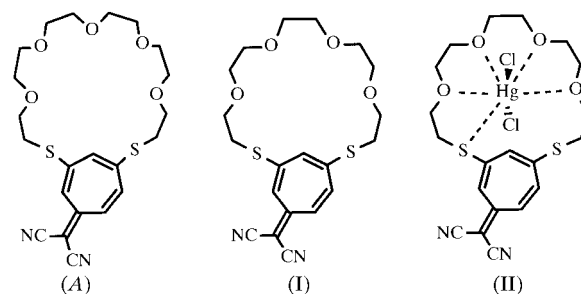
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The structures of the title compound, $C_{20}H_{24}N_2O_4S_2$, and its mercury(II) dichloride complex, dichloro[20-dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricoso-1(23),-18,21-triene- $\kappa^4O,\kappa S^{17}$]mercury(II), $[HgCl_2(C_{20}H_{24}N_2O_4S_2)]$, have been determined by X-ray crystallographic analyses. The mercury(II) dichloride complex has two independent molecules of $[HgCl_2(C_{20}H_{24}N_2O_4S_2)]$ in the lattice. The mercury(II) ion has pentagonal bipyramidal coordination which involves one S atom, four O atoms and two Cl^- ions.

Comment

The development of selective ion recognition systems has been of much concern as a solution to environmental pollution (Bacon & Kirch, 1985, 1987; Izatt, Bruening *et al.*, 1985; Izatt, Clark & Christensen, 1985; Izatt *et al.*, 1986; Parham & Shamsipur, 1994). Thiocrown ethers can be used as extraction agents for heavy-metal ions (Dalley & Larson, 1981; Blake & Schröder, 1990; Sibert *et al.*, 1994). Recently, we have reported the synthesis and the complexation of mercuriphilic dithiocrown ethers with tropone and heptafulvene chromophores (Kubo *et al.*, 1995, 1996; Kato *et al.*, 1995; Mori *et al.*, 1996, 1997, 1998), in which the carbonyl or dicyanomethylene groups played an important role in the selective complexation and transport of the mercury(II) ion. The structures of the mercury(II) dichloride complexes were elucidated by X-ray crystallographic analyses (Kubo *et al.*, 1995, 1996, 1998; Kato *et al.*, 1995; Mori *et al.*, 1996, 1997, 1998). The most effective mercuriphilic dithiocrown ether, 23-dicyanomethylene-5,8,11,14,17-pentaoxa-2,20-dithiabicyclo[19.4.1]hexacoso-1(26),21,24-triene, (A), showed preferential coordination of the mercury(II) ion to O over S atoms (Kubo *et al.*, 1998). In order to determine the precise coordination structure, single crystals of 20-dicyanomethylene-5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricoso-1(23),18,21-triene, (I), and its

mercury(II) dichloride complex, (II), have now been investigated by X-ray crystallographic analyses.



In title compound (I), the dicyanomethylene group is out of the crown ether ring, which has the conformation $S_tC_gC_tO_gC_gC_gO_tC_tC_tO_tC_gC_tO_tC_gC_gS$, where *t* and *g* denote *trans* and *gauche* linkages, respectively. The planarity of the 8,8-dicyanoheptafulvene ring system is fairly good; the dihedral angle between the least-squares planes *A* defined by C1, C2, C3, C4, C5, C6 and C7, and *B* defined by C8, C9, C10, N1 and N2 is $4.7(1)^\circ$. The exocyclic C=C bond length [C1—C8 1.397(3) Å] of (I) is similar to those [1.389(3) and 1.392(5) Å] of 5- and 7-(dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithianes (Kubo *et al.*, 1994) and is shorter than that [1.422(13) Å] of 8,8-dicyanoheptafulvene (Shimanouchi *et al.*, 1966).

The mercury(II) dichloride complex, (II), has two independent structures, (IIa) and (IIb), in the lattice. The mercury(II) ions are surrounded by one S atom, four O atoms and two Cl^- ions in a pentagonal bipyramidal coordination. The conformation of the dithiocrown ether part is $S_tC_gC_tO_tC_gC_tO_tC_gC_tO_tC_tC_gS$. All the CH_2-O bonds have *trans* conformations. The geometry is similar to that observed in the

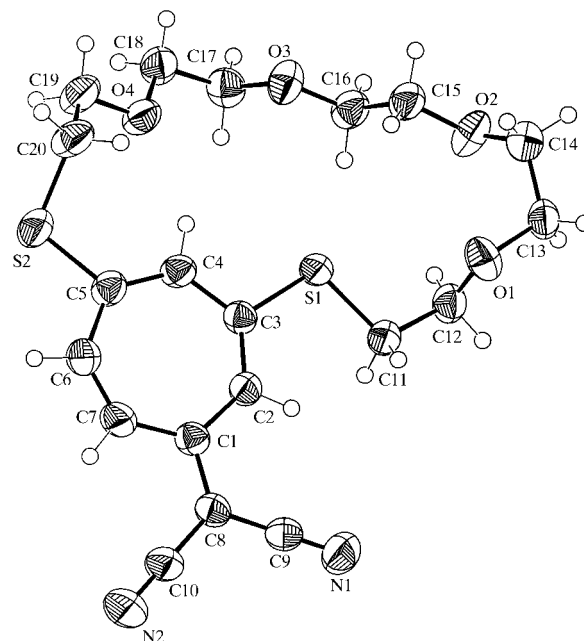


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.

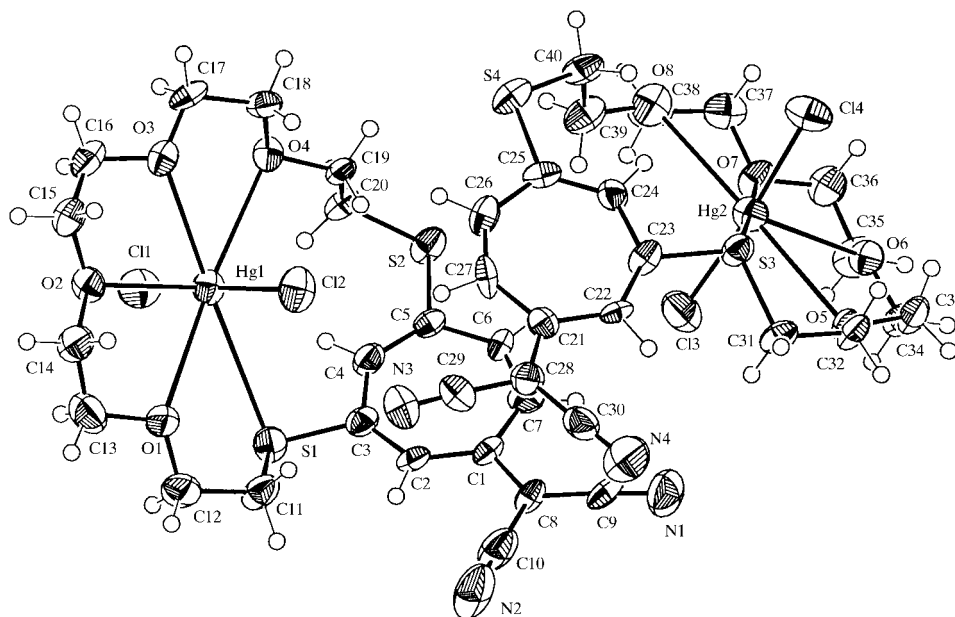


Figure 2
The molecular structure of (II) showing 50% probability displacement ellipsoids.

mercury(II) dichloride complex of 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricoso-1(22),18,20-trien-23-one (Kubo *et al.*, 1996). The mercury(II) dichloride is inserted perpendicular to the crown ring: the angles between the least-squares planes of mercury(II) dichloride [(IIa) Cl1–Hg1–Cl2, (IIb) Cl3–Hg2–Cl4] and the thiocrown planes [(IIa) S1–O1–O2–O3–O4, (IIb) S3–O5–O6–O7–O8] are 92.6 (1)° for (IIa) and 92.3 (2)° for (IIb). The bond angles for Cl–Hg–Cl are 168.43 (13) and 173.18 (14)°, respectively, which are smaller by 6–10° than the reported angle [178.9 (5)°] of HgCl₂ (Subramanian & Seff, 1980). The distances for Hg–O are 2.677–2.977 Å for (IIa) and 2.605–3.083 Å for (IIb), which are similar to those found in the mercury dichloride complexes of tetraethylene glycol dimethyl ether (2.78–2.96 Å; Iwamoto, 1973) and 5,8,11,14-tetraoxa-2,17-dithiabicyclo[16.4.1]tricoso-1(22),18,20-trien-23-one (2.774–2.860 Å; Kubo *et al.*, 1996). The planarity of the heptafulvene ring changed slightly by complexation with mercury(II) dichloride; the angle between planes A and B is 3.3 (6)° for (IIa) and 7.9 (7)° for (IIb), while that of (I) is 4.7 (1)°. The S2 and S4 atoms are not coordinated with mercury(II) ions. The Hg–S distances [5.258 (4) for (IIa), 5.360 (4) Å for (IIb)] are much longer than the typical distances for Hg–S (2.50–2.75 Å; Alcock *et al.*, 1978; Sato *et al.*, 1989; Dalley & Larson, 1981; Sibert *et al.*, 1994). As a result, an electron-withdrawing 8,8-dicyanoheptafulvene moiety would reduce the affinity of the S atom for the mercury(II) ion.

Experimental

The single crystals of the title compound, (I), were obtained by crystallization of (I) from CH₃CN and those of the complex (II) were obtained by crystallization of an equimolar mixture of (I) and HgCl₂ from CH₃CN.

Compound (I)

Crystal data

C₂₀H₂₄N₂O₄S₂

M_r = 420.53

Triclinic, *P*1

a = 10.947 (5) Å

b = 12.185 (5) Å

c = 8.883 (5) Å

α = 103.808 (5)°

β = 113.331 (5)°

γ = 76.135 (5)°

V = 1042.5 (9) Å³

Z = 2

D_x = 1.340 Mg m⁻³

Cu *K*α radiation

Cell parameters from 25 reflections

θ = 19.15–42.78°

μ = 2.555 mm⁻¹

T = 296 (2) K

Prism, red

0.50 × 0.30 × 0.10 mm

Data collection

Enraf–Nonius FR590 diffractometer

ω–2θ scans

Absorption correction: empirical via ψ scans (North *et al.*, 1968)

T_{min} = 0.473, *T_{max}* = 0.775

4032 measured reflections

3550 independent reflections

3249 reflections with *I* > 2σ(*I*)

R_{int} = 0.014

θ_{max} = 64.91°

h = –11 → 12

k = –13 → 14

l = –10 → 0

3 standard reflections

frequency: 120 min
intensity decay: none

Table 1

Selected geometric parameters (Å, °) for (I).

S1–C3	1.7586 (18)	C2–C3	1.368 (3)
S2–C5	1.7572 (19)	C3–C4	1.432 (3)
N1–C9	1.146 (3)	C4–C5	1.359 (3)
N2–C10	1.141 (3)	C5–C6	1.441 (3)
C1–C8	1.397 (3)	C6–C7	1.339 (3)
C1–C2	1.420 (2)	C8–C9	1.421 (3)
C1–C7	1.434 (3)	C8–C10	1.423 (3)
C3–S1–C11–C12	173.66 (13)	O2–C15–C16–O3	174.74 (16)
C13–O1–C12–C11	–176.08 (16)	C16–O3–C17–C18	173.34 (16)
S1–C11–C12–O1	69.71 (18)	C19–O4–C18–C17	176.71 (18)
C12–O1–C13–C14	105.8 (2)	O3–C17–C18–O4	–67.9 (2)
C15–O2–C14–C13	119.9 (2)	C18–O4–C19–C20	–166.48 (19)
O1–C13–C14–O2	–65.6 (2)	O4–C19–C20–S2	–77.3 (2)
C14–O2–C15–C16	–168.79 (17)	C5–S2–C20–C19	101.45 (17)
C17–O3–C16–C15	–178.89 (16)		

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.104$
 $S = 1.101$
 3550 reflections
 254 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.3471P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0120 (8)

Compound (II)

Crystal data

$[\text{HgCl}_2(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2)]$
 $M_r = 692.02$
 Monoclinic, $P2_1/a$
 $a = 15.387(5) \text{ \AA}$
 $b = 22.349(5) \text{ \AA}$
 $c = 14.579(5) \text{ \AA}$
 $\beta = 95.337(5)^\circ$
 $V = 4992(3) \text{ \AA}^3$
 $Z = 8$

$D_x = 1.842 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation
 Cell parameters from 22 reflections
 $\theta = 19.93\text{--}42.14^\circ$
 $\mu = 14.840 \text{ mm}^{-1}$
 $T = 296(2) \text{ K}$
 Prism, red
 $0.15 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Enraf–Nonius FR590 diffractometer
 ω – 2θ scans
 Absorption correction: empirical via ψ scans (North *et al.*, 1968)
 $T_{\min} = 0.179$, $T_{\max} = 0.227$
 8840 measured reflections
 8483 independent reflections
 4883 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$
 $\theta_{\max} = 64.98^\circ$
 $h = -18 \rightarrow 18$
 $k = -26 \rightarrow 0$
 $l = 0 \rightarrow 17$
 3 standard reflections
 frequency: 120 min
 intensity decay: 6.4%

Table 2

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

Hg1–Cl1	2.294 (3)	N4–C30	1.158 (17)
Hg1–Cl2	2.295 (3)	C1–C8	1.403 (14)
Hg1–O2	2.677 (8)	C1–C2	1.411 (15)
Hg1–O3	2.725 (8)	C1–C7	1.443 (16)
Hg1–O4	2.969 (8)	C2–C3	1.348 (15)
Hg1–O1	2.978 (8)	C3–C4	1.439 (16)
Hg1–S1	3.268 (3)	C4–C5	1.374 (16)
Hg2–Cl3	2.307 (4)	C5–C6	1.426 (15)
Hg2–Cl4	2.314 (3)	C6–C7	1.363 (16)
Hg2–O6	2.606 (8)	C8–C10	1.408 (19)
Hg2–O7	2.661 (8)	C8–C9	1.410 (17)
Hg2–O8	2.913 (9)	C21–C28	1.382 (16)
Hg2–O5	3.083 (8)	C21–C27	1.434 (16)
Hg2–S3	3.138 (3)	C21–C22	1.456 (15)
S1–C3	1.770 (12)	C22–C23	1.348 (15)
S2–C5	1.750 (12)	C23–C24	1.430 (15)
S3–C23	1.755 (12)	C24–C25	1.374 (16)
S4–C25	1.738 (12)	C25–C26	1.453 (17)
N1–C9	1.129 (16)	C26–C27	1.319 (17)
N2–C10	1.121 (17)	C28–C30	1.403 (19)
N3–C29	1.124 (16)	C28–C29	1.424 (18)
Cl1–Hg1–Cl2	168.43 (13)	Cl3–Hg2–Cl4	173.18 (14)
O2–Hg1–O3	62.1 (2)	O6–Hg2–O7	65.1 (3)
O3–Hg1–O4	61.1 (2)	O7–Hg2–O8	62.3 (3)
O2–Hg1–O1	61.2 (2)	O6–Hg2–O5	61.1 (2)
O1–Hg1–S1	58.76 (18)	O5–Hg2–S3	58.06 (16)
O4–C19–C20–S2	–167.4 (7)	O8–C39–C40–S4	–163.7 (8)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.137$
 $S = 1.009$
 8483 reflections
 559 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.06 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.48 \text{ e } \text{\AA}^{-3}$

All H atoms were calculated at ideal positions and restrained to ride on the atom to which they are bonded. Isotropic displacement factors of H atoms were fixed to 1.2 times U_{eq} of the riding atoms.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1020). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W., Heeron, N. & Moore, P. (1978). *J. Chem. Soc. Dalton Trans.* pp. 394–399.
- Altomare, A., Burla, M. C., Camalli, M., Casciarano, 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.
- Blake, A. J. & Schröder, M. (1990). *Adv. Inorg. Chem.* **35**, 1–80.
- Dalley, N. K. & Larson, S. B. (1981). *Acta Cryst.* **B37**, 2225–2227.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
- Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.
- Iwamoto, R. (1973). *Bull. Chem. Soc. Jpn.* **46**, 1114–1118, 1118–1123, 1123–1127.
- Izatt, R. M., Bruening, R. L., Clark, G. A., Lamb, J. D. & Christensen, J. J. (1985). *J. Membr. Sci.* **28**, 77–86.
- Izatt, R. M., Clark, G. A. & Christensen, J. J. (1985). *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., Mori, A., Kato, N. & Takeshita, H. (1996). *Acta Cryst.* **C52**, 1656–1658.
- Kubo, K., Mori, A., Kato, N. & Takeshita, H. (1998). *Heterocycles*, **49**, 385–392.
- Kubo, K., Mori, A., Takeshita, H. & Tsuzuki, H. (1994). *Acta Cryst.* **C50**, 603–606.
- 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.* **A24**, 351–359.
- Parham, H. & Shamsipur, M. (1994). *J. Membr. Sci.* **86**, 29–35.
- Sato, S., Habata, Y., Sato, M. & Akabori, S. (1989). *Bull. Chem. Soc. Jpn.* **62**, 3963–3967.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shimanouchi, H., Ashida, T., Sasada, Y., Kakudo, M., Murata, I. & Kitahara, Y. (1966). *Bull. Chem. Soc. Jpn.* **39**, 2322–2331.
- Sibert, J. W., Lange, S. J., Stern, C., Hoffman, B. M. & Barrett, A. G. M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 564–566.
- Subramanian, V. & Seff, K. (1980). *Acta Cryst.* **B36**, 2132–2135.