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Di-μ-sulfido-bis[diaqua(18-crown-6)-barium(II)]–saccharin (1/2)

Suchada Chantrapromma,[a] Anwar Usman[b] and Hoong-Kun Fun[b]*

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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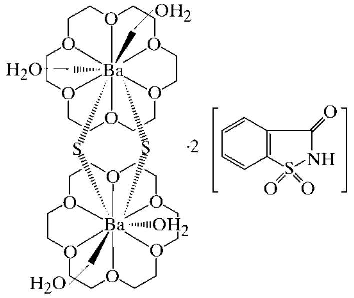
The molecule of the title compound {systematic name: di-μ-sulfido-bis[diaqua(1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)-barium(II)] bis[1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide]}, $[Ba_2S_2(C_{12}H_{24}O_6)_2(H_2O)_4](C_7H_5NO_3S)_2$, lies on an inversion centre. The Ba^{II} atom encapsulated by the 18-crown-6 ring is coordinated by the six O atoms of the crown, two water O atoms and two bridging S atoms. The four-membered ring composed of the Ba^{II} atoms and the bridging S atoms makes a dihedral angle of 67.1 (1)° with the crown-ether ring. The aromatic ring system of the saccharin moiety is essentially planar. The packing is built up from layers of the molecules and is stabilized by three intermolecular O—H$\cdots$O hydrogen bonds.

Comment

Complexes of alkaline earth metal cations with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) have been investigated intensively (Dyer *et al.*, 1986; Wei *et al.*, 1988; Luger *et al.*, 1992; Rheingold *et al.*, 1993; Usman *et al.*, 2002). Generally, these studies have been devoted to the structures of the complexes, including the conformation of the macrocycle and the position of the metal cation relative to the crown centre, due to the different nature of the metal cation and the counter-anion.

In continuing our study of the variation with temperature of the cell parameters of barium–18-crown-6 complexes, we have prepared the title complex, (I), which is a 2:2 complex of diaqua(18-crown-6)barium(II) sulfide and saccharin. However, for this complex, the cell parameters are almost constant in the temperature range 183–300 K. An X-ray crystal structure determination of (I) was undertaken at 293 K, and the results are reported here.



(I)

The asymmetric unit of (I) contains only one half of the molecule; the other half is generated by a centre of inversion. The Ba^{II} atom is encapsulated by an 18-crown-6 ring and is

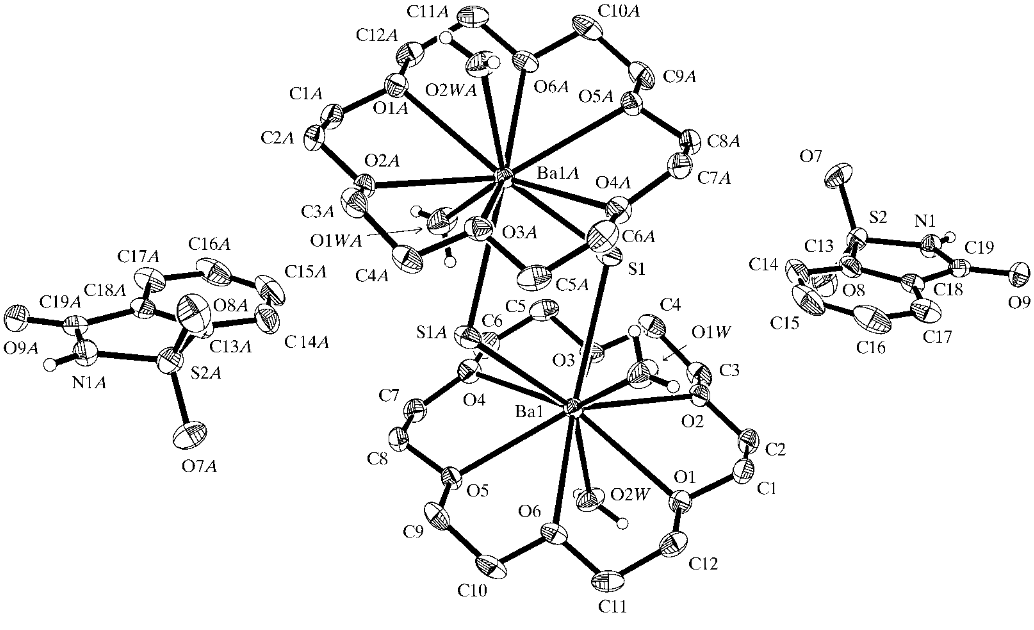


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms attached to C atoms have been omitted. [Symmetry code: (*A*) $-x, -y, 1 - z$.]

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coordinated to the six O atoms of the crown, two water O atoms and two bridging S atoms. The atomic numbering scheme and molecular conformation of (I) are shown in Fig. 1. The bond lengths and angles have normal values (Allen *et al.*, 1987).

The average Ba—O$_{crown}$ distance is 2.90 (2) Å, which is slightly elongated compared with that in barium–bis(trimethylacetate)–18-crown-6 [2.828 (11) Å; Rheingold *et al.*, 1993] or barium–2,4-dinitrophenolate–18-crown-6 [2.80 (5) Å; Usman *et al.*, 2002]. The average Ba—O$_{water}$ distance [2.83 (2) Å] is comparable with that in aqua(18-crown-6)-bis(*o*-nitrophenolato)barium(II) [2.836 (4) Å; Chantrapromma *et al.*, 2002].

The aromatic ring systems of the saccharin moieties in (I) are essentially planar, with a maximum deviation of 0.042 (4) Å for atom C19, and the dihedral angle between the five- and six-membered rings is 2.2 (2)°. The bond lengths and angles within this moiety are comparable with those in free saccharin (Deng *et al.*, 2001). Atom O9 is displaced by 0.153 (3) Å from the saccharin plane, whereas atoms O7 and O8 are conditioned by the tetrahedral conformation of the S2 atom, with the average angle subtended at S2 being 109.2°.

In the crown of (I), the C atoms deviate from the least-squares plane by between −0.352 (4) and 0.443 (5) Å, with the Ba^{II} atom displaced from the crown ring by 0.908 (1) Å. The average C—O and C—C bond distances are 1.426 and 1.486 Å, respectively. The average C—O distance is normal for a C—O single bond (Allen *et al.*, 1987), whereas that of the C—C bond is shorter than the average for a Csp^3—Csp^3 single bond, due to the macrocyclic C—C shortening of the crown ether (Shoham *et al.*, 1983).

The O—C—C and C—O—C angles are almost tetrahedral, with average values of 108.7 and 111.8°, respectively. The O atoms of the crown ring form a regular hexagon, with non-bonded O···O distances in the range 2.766 (4)–2.824 (4) Å, with maximum deviations from the mean plane of 0.12 and −0.28 Å for atoms O3 and O4.

The conformation of the crown in (I) is that of the typical crown-ether arrangement, *i.e.* approximate D_{3d} symmetry, determined by the +*sc* or −*sc* and *ap* conformations of the O—C—C—O and C—O—C—C torsion angles. The mean plane of the crown makes a dihedral angle of 67.1 (1)° with respect to the Ba1/Ba1*A*/S1/S1*A* plane.

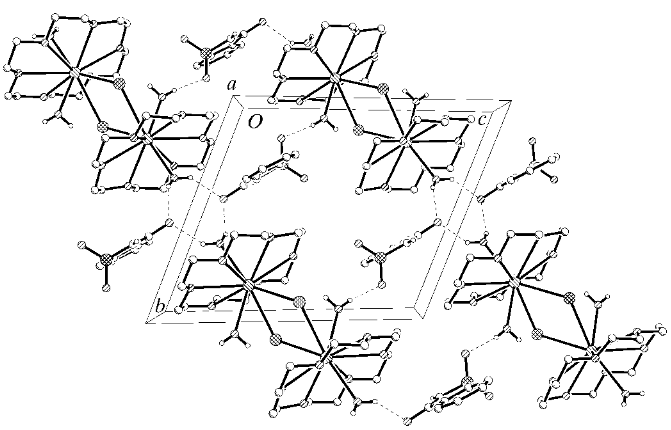

Figure 2
A packing diagram for (I), viewed down the *a* axis. H atoms attached to C atoms have been omitted.

Symmetry-related molecules are linked by intermolecular O2*W*—H1*W*2···O9^{ii} and O2*W*—H2*W*2···O9^{iii} hydrogen bonds into columns, which are interconnected by O1*W*—H1*W*1···O8^{i} hydrogen bonds into molecular layers (Fig. 2).

Experimental

The title complex was prepared by thoroughly mixing Ba(OH)$_2$·8H$_2$O (1.58 g, 5 mmol), sodium saccharinate (2.05 g, 10 mmol) and 18-crown-6 (1.32 g, 5 mmol) in ethanol (50 ml). Distilled water (5 ml) was then added and the mixture warmed until all the solid had dissolved. The solution was filtered and left to evaporate slowly in air. Colourless single crystals of (I) suitable for X-ray analysis were obtained after a few days.

Crystal data

$[Ba_2S_2(C_{12}H_{24}O_6)_2(H_2O)_4]$-$(C_7H_5NO_3S)_2$
M_r = 1305.85
Triclinic, $P\bar{1}$
a = 8.5668 (5) Å
b = 11.9073 (6) Å
c = 14.0768 (8) Å
α = 109.195 (1)°
β = 103.383 (1)°
γ = 96.374 (1)°
V = 1291.6 (1) Å^3
Z = 1
D_x = 1.679 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6797 reflections
θ = 2.6–28.3°
μ = 1.75 mm^{-1}
T = 293 (2) K
Block, colourless
0.28 × 0.26 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.639, T_{max} = 0.678
8231 measured reflections
6090 independent reflections
5704 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 28.3°
h = −11 → 8
k = −15 → 15
l = −13 → 18

Table 1
Selected geometric parameters (Å, °).

Ba1—S1^i	3.1904 (10)	Ba1—S1	3.2391 (10)
C12—O1—C1—C2	−169.3 (3)	C6—O4—C7—C8	−178.7 (3)
C3—O2—C2—C1	172.1 (3)	C9—O5—C8—C7	174.1 (3)
O1—C1—C2—O2	−60.5 (4)	O4—C7—C8—O5	61.2 (4)
C2—O2—C3—C4	176.6 (3)	C8—O5—C9—C10	−168.9 (3)
C5—O3—C4—C3	177.2 (3)	C11—O6—C10—C9	176.6 (3)
O2—C3—C4—O3	65.1 (4)	O5—C9—C10—O6	−64.0 (5)
C4—O3—C5—C6	−165.9 (3)	C10—O6—C11—C12	179.9 (3)
C7—O4—C6—C5	175.7 (3)	C1—O1—C12—C11	172.7 (3)
O3—C5—C6—O4	−65.8 (4)	O6—C11—C12—O1	63.0 (4)

Symmetry code: (i) −*x*, −*y*, 1 − *z*.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O8^i	0.85	2.05	2.898 (7)	170
O2*W*—H1*W*2···O9^{ii}	0.85	2.12	2.822 (4)	140
O2*W*—H2*W*2···O9^{iii}	0.85	2.16	2.915 (5)	147

Symmetry codes: (i) −*x*, −*y*, 1 − *z*; (ii) *x*, *y*, 1 + *z*; (iii) 1 − *x*, 1 − *y*, 1 − *z*.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 2.0593P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.102$	$\Delta\rho_{\max} = 2.18$ e Å^{-3}
$S = 1.10$	$\Delta\rho_{\min} = -0.74$ e Å^{-3}
6090 reflections	
307 parameters	
H-atom parameters constrained	

All H atoms were fixed geometrically with ideal bond lengths and angles, and were treated as riding atoms. The highest peak of 2.18 e Å^{-3} and deepest hole of -0.74 e Å^{-3} were 0.78 and 0.53 Å from Ba1, 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1115). Services for accessing these data are described at the back of the journal.

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