

were constrained to equal the respective F-atom values. The remaining non-H atoms were refined anisotropically. Pyridine H atoms were fixed at ideal positions with isotropic displacement parameters equal to 1.2 times the value of the C atom to which it is bonded. For (I), the H atoms on the water molecules, associated with O7 and O8 were not located. Neutral atom scattering factors were taken from Cromer & Waber (1974).

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *DIRDIF94* (Beurskens *et al.*, 1994) for (I); *DIRDIF92* (Beurskens *et al.*, 1992) for (II). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structures: *SAP91* (Fan, 1991) for (I); *SHELXS86* (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Bis(barium disaccharinate triglyme)†

CHRISTIAN NÄTHER, TIM HAUCK AND HANS BOCK

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany. E-mail: bock@bock.anorg.chemie.uni-frankfurt.de

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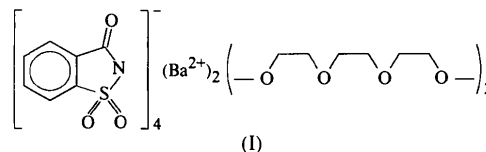
Abstract

The crystal structure of [Ba(C₇H₄NO₃S)₂(C₈H₁₈O₄)₂] has been determined at 150 K. The structure contains dimers of barium disaccharinate, in which each barium dication is surrounded by three saccharinate anions and one triglyme molecule. The asymmetric unit contains two crystallographically independent saccharinate anions, of which one is coordinated to the barium dication by both sulfonyl O atoms, whereas both are coordinated *via* their amide groups. With four additional contacts to the triglyme O atoms, the Ba²⁺ centres achieve a tenfold coordination sphere.

Comment

Detailed structure investigations of crystalline organo-barium complexes are rather rare, presumably due to the difficulties associated with their preparation caused by the low reactivity of barium metal. The saccharinate anion was selected because of its excellent complexation properties. The numerous structures of saccharinate salts reported in the literature usually contain transition metal ions and only a few structures containing alkaline or alkaline earth cations are reported. Representative examples are magnesium disaccharinate heptahydrate, sodium saccharinate 2/3-hydrate (Jovanovski & Kamenar, 1982) or dipotassium sodium trisaccharinate monohydrate (Malik, Haider, Hossain & Hursthouse, 1984).

The title compound, (I), crystallizes as a dimeric complex composed of two barium dications, four saccharinate anions and two triglyme molecules. Each barium centre is surrounded by three saccharinate anions and one triglyme molecule. Two of the saccharinate anions coordinate *via* their amide groups and the third *via* the sulfonyl O atoms. The barium dication is located within an irregular polyhedron and exhibits coordination num-



† Alternative name: bis{[bis{1,2-benzisothiazol-3(2H)-onate 1,1-dioxide}(2,5,8,11-tetraoxadodecane)}barium}.

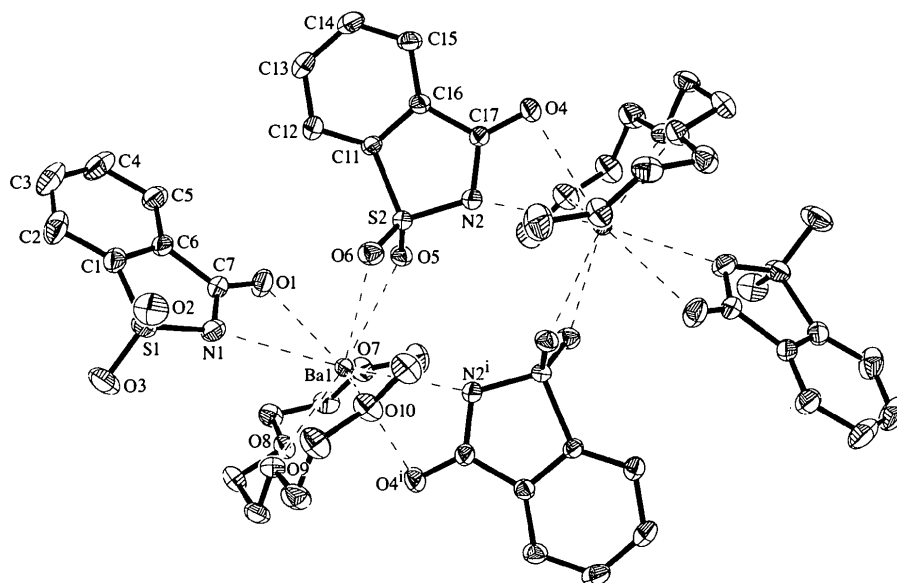


Fig. 1. The structure of bis(barium disaccharinate triglyme) with the atomic labelling. The barium coordination is indicated by dashed lines. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

ber 10. Both the eight Ba \cdots O contact distances between 2.741 (2) and 2.945 (2) Å, and the two Ba \cdots N contact distances of 2.848 (2) and 2.995 (2) Å are within the expected ranges.

The saccharinate anion is planar with the most significant deviations in the two independent molecules amounting to 0.035 (2) and 0.045 (2) Å. Their bond lengths and angles are comparable within experimental error with those in saccharine itself (Bart, 1968; Okaya, 1969), with the exceptions of the C—N and N—S bond lengths, which are shortened to 1.343 (3), 1.365 (3), 1.620 (2) and 1.598 (2) Å, and the C—N—S angle which is narrowed to 111.3 (2) or 111.61 (15)°. These structural changes can be traced to the additional charge localized on the nitrogen centre.

Experimental

Saccharin (saccharide benzoic acid–sulfimide) is commercially available from Fluka. For the preparation of the complex, barium granulate (274 mg, 2 mmol) was surface cleaned by ultrasonic treatment and transferred under argon into a vacuum-dried Schlenk trap. In an argon atmosphere, aprotic triglyme (20 ml) and saccharin (184 mg, 1 mmol) were added. After 3 d, the resulting colourless solution was covered with a layer of 5 ml dry *n*-hexane and within 2 d, colourless air- and moisture-sensitive crystals had grown.

Crystal data

[Ba(C₇H₄NO₃S)₂-
(C₈H₁₈O₄)₂]₂
M_r = 1359.82
Triclinic
P $\bar{1}$

Mo *K*α radiation
 λ = 0.71073 Å
Cell parameters from 60
reflections
 θ = 8–16°

a = 8.4068 (4) Å
b = 11.4513 (5) Å
c = 14.9166 (6) Å
 α = 76.375 (3)°
 β = 81.461 (3)°
 γ = 71.342 (3)°
V = 1318.07 (10) Å³
Z = 1
D_x = 1.713 Mg m⁻³
D_m not measured

μ = 1.722 mm⁻¹
T = 150 (2) K
Plate
0.40 × 0.40 × 0.08 mm
Colourless

Data collection

Siemens *P4* diffractometer
 ω scan
Absorption correction:
face-indexed (*XPREP*;
Siemens, 1996)
T_{min} = 0.53, *T_{max}* = 0.87
10 571 measured reflections
9997 independent reflections
8992 reflections with
I > 2σ(*I*)

R_{int} = 0.017
 θ_{\max} = 33.50°
h = 0 → 12
k = -16 → 17
l = -22 → 23
4 standard reflections
every 400 reflections
intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.030
wR (*F*²) = 0.075
S = 1.061
9997 reflections
335 parameters
H atoms: see below
w = 1/[σ²(*F_o*²) + (0.0265*P*)²
+ 1.7198*P*]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.869 e Å⁻³
Δρ_{min} = -0.825 e Å⁻³
Extinction correction:
SHELXL93 (Sheldrick,
1993)
Extinction coefficient:
0.0024 (5)
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	<i>U</i> _{eq}
Ba1	0.383679 (14)	0.000292 (11)	0.214799 (8)	0.01764 (4)
S1	0.12012 (8)	0.33320 (6)	0.35348 (4)	0.03023 (11)
O1	0.5357 (2)	0.1509 (2)	0.27214 (14)	0.0351 (4)
O2	-0.0002 (3)	0.4130 (2)	0.2886 (2)	0.0439 (5)
O3	0.0499 (3)	0.2870 (2)	0.4441 (2)	0.0482 (5)
N1	0.2534 (3)	0.2194 (2)	0.3100 (2)	0.0308 (4)
C1	0.2670 (3)	0.4096 (2)	0.3645 (2)	0.0289 (4)
C2	0.2472 (4)	0.5155 (3)	0.3999 (2)	0.0424 (6)
C3	0.3920 (5)	0.5510 (3)	0.3982 (2)	0.0498 (8)
C4	0.5481 (5)	0.4832 (3)	0.3649 (2)	0.0462 (7)
C5	0.5665 (4)	0.3758 (2)	0.3314 (2)	0.0337 (5)
C6	0.4225 (3)	0.3407 (2)	0.33174 (14)	0.0256 (4)
C7	0.4106 (3)	0.2286 (2)	0.3013 (2)	0.0264 (4)
S2	0.54351 (6)	0.17306 (5)	0.02100 (3)	0.01965 (8)
O4	0.6980 (3)	0.2292 (2)	-0.22147 (11)	0.0329 (4)
O5	0.6417 (2)	0.06171 (15)	0.08081 (10)	0.0241 (3)
O6	0.3676 (2)	0.2105 (2)	0.05516 (12)	0.0272 (3)
N2	0.5690 (3)	0.1554 (2)	-0.08385 (12)	0.0250 (3)
C11	0.6325 (3)	0.2978 (2)	0.00359 (14)	0.0205 (3)
C12	0.6501 (3)	0.3649 (2)	0.0656 (2)	0.0251 (4)
C13	0.7304 (3)	0.4578 (2)	0.0306 (2)	0.0307 (4)
C14	0.7899 (3)	0.4805 (2)	-0.0620 (2)	0.0319 (5)
C15	0.7707 (3)	0.4117 (2)	-0.1231 (2)	0.0273 (4)
C16	0.6908 (3)	0.3193 (2)	-0.08868 (14)	0.0217 (3)
C17	0.6546 (3)	0.2325 (2)	-0.13926 (14)	0.0240 (4)
O7	0.6926 (2)	-0.1701 (2)	0.27442 (12)	0.0293 (3)
O8	0.4163 (2)	-0.1405 (2)	0.39619 (11)	0.0273 (3)
O9	0.0946 (2)	-0.0056 (2)	0.33593 (11)	0.0256 (3)
O10	0.0781 (2)	0.0620 (2)	0.14379 (12)	0.0313 (3)
C21	0.8110 (4)	-0.2443 (3)	0.2153 (2)	0.0435 (6)
C22	0.7099 (3)	-0.2252 (2)	0.3698 (2)	0.0309 (4)
C23	0.5724 (3)	-0.1454 (3)	0.4255 (2)	0.0304 (4)
C24	0.2729 (3)	-0.0999 (3)	0.4583 (2)	0.0322 (5)
C25	0.1216 (3)	-0.1018 (2)	0.4171 (2)	0.0301 (4)
C26	-0.0493 (3)	0.0011 (3)	0.2927 (2)	0.0357 (5)
C27	-0.0668 (3)	0.1009 (3)	0.2060 (2)	0.0353 (5)
C28	0.0520 (3)	0.1254 (3)	0.0501 (2)	0.0341 (5)

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTLPC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93 CIFTAB.

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 Siemens (1996). *SHELXTLPC*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Table 2. Selected geometric parameters (Å, °)

Ba1—O10	2.741 (2)	S1—C1	1.772 (3)
Ba1—O1	2.787 (2)	O1—C7	1.239 (3)
Ba1—O8	2.807 (2)	N1—C7	1.343 (3)
Ba1—O9	2.814 (2)	S2—O6	1.450 (2)
Ba1—O7	2.823 (2)	S2—O5	1.453 (2)
Ba1—O5	2.867 (2)	S2—N2	1.598 (2)
Ba1—O6	2.945 (2)	S2—C11	1.766 (2)
Ba1—N1	2.995 (2)	O4—C17	1.232 (3)
S1—O2	1.441 (2)	O4—Ba1'	2.898 (2)
S1—O3	1.442 (2)	N2—C17	1.365 (3)
S1—N1	1.620 (2)	N2—Ba1'	2.848 (2)
O2—S1—O3	115.73 (14)	O6—S2—O5	112.08 (10)
O2—S1—N1	111.41 (13)	O6—S2—N2	112.80 (11)
O3—S1—N1	111.21 (13)	O5—S2—N2	111.14 (10)
O2—S1—C1	110.59 (12)	O6—S2—C11	111.52 (10)
O3—S1—C1	109.48 (13)	O5—S2—C11	110.98 (10)
N1—S1—C1	96.81 (11)	N2—S2—C11	97.49 (10)
C7—N1—S1	111.3 (2)	C17—N2—S2	111.61 (15)
C6—C1—S1	106.8 (2)	C16—C11—S2	106.86 (15)
C2—C1—S1	131.4 (2)	C12—C11—S2	130.3 (2)
O1—C7—N1	123.7 (2)	O4—C17—N2	122.9 (2)
O1—C7—C6	122.4 (2)	O4—C17—C16	124.4 (2)
N1—C7—C6	113.9 (2)	N2—C17—C16	112.7 (2)

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

All H atoms were positioned in idealized geometry and refined with individual isotropic displacement parameters using the riding model, with phenyl C—H 0.93, methylene C—H 0.97 and methyl C—H 0.96 Å.

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Bis(μ-bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarboxylato-κ²O,O':κ²O'',O''')bis-[aqua(2,2'-bipyridine-*N,N'*)manganese(II)] Monohydrate

UTE BAUMEISTER AND HELMUT HARTUNG

Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany.
E-mail: baumeister@chemie.uni-halle.de

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Abstract

The title compound, [Mn(μ-C₉H₈O₄)(C₁₀H₈N₂)(H₂O)]₂·H₂O, exists in the crystal as a cyclic dimer about an inversion centre. Two Mn²⁺ ions are double bridged by two bicyclic dianions which act as tetradentate ligands.