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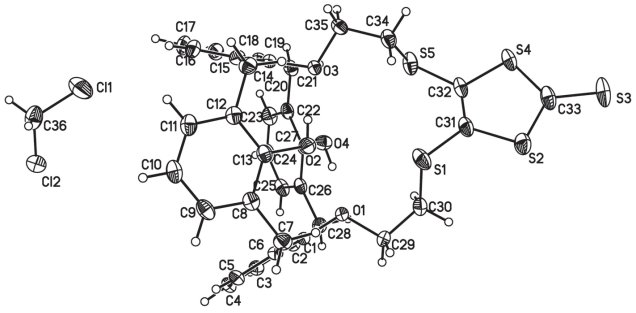
The crystal structure of 25,27-(2,2′-[(2-thioxo-1,3-dithiole-4,5-diyl)disulfanediyl]diethanolate)-26,28-dihydroxycalix[4]arene — dichloromethane (1/1), $C_{36}H_{32}Cl_2O_4S_5$



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Abstract

$C_{36}H_{32}Cl_2O_4S_5$, orthorhombic, *Pccn* (no. 56), $a = 15.4426(11)$ Å, $b = 17.4623(13)$ Å, $c = 25.9153(19)$ Å, $V = 6988.4(9)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0590$, $wR_{ref}(F^2) = 0.1958$, $T = 291(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

A suspension of 25,27-bis(2-bromoethoxy)-26,28-dihydroxycalix[4]arene [4] (1.9 g, 3 mmol) and bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dithiol)zincate [5] (1.5 g, 2.1 mmol) was refluxed for 20 h in acetonitrile (300 mL) under a nitrogen atmosphere. After the removal of the solvent, the residue was dissolved in methylene chloride (100 mL) and washed with water, and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography with dichloromethane/petroleum ether (2:3) to give the title compound (49% yield) as a yellow powder [6]. Single crystals were obtained by slow evaporation from a dichloromethane and petroleum ether solution at room temperature.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.38 × 0.27 × 0.13 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.52 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	42129, 8015, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4993
$N(param)_{refined}$:	426
Programs:	Bruker programs [1, 2], SHELX [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.75994(12)	0.63585(11)	0.31194(7)	0.1412(6)
Cl2	0.87877(9)	0.67621(8)	0.23222(7)	0.1163(5)
S1	0.31810(6)	1.09516(8)	0.40616(4)	0.0810(3)
S2	0.14302(7)	1.16296(7)	0.42987(4)	0.0782(3)
S3	−0.04293(7)	1.15954(9)	0.45992(5)	0.1062(5)
S4	0.05758(6)	1.01733(7)	0.43961(4)	0.0721(3)
S5	0.21069(6)	0.92363(7)	0.40802(4)	0.0745(3)
O1	0.46017(14)	1.07698(12)	0.33079(9)	0.0578(6)
O2	0.51328(14)	0.99620(14)	0.42124(10)	0.0638(6)
H2	0.4856	0.9570	0.4267	0.096*
O3	0.40043(13)	0.86555(12)	0.41801(8)	0.0499(5)
O4	0.39416(16)	0.93281(12)	0.32067(8)	0.0574(6)
H4	0.4040	0.9782	0.3150	0.086*
C1	0.53234(19)	1.06803(15)	0.29898(12)	0.0466(7)
C2	0.52000(19)	1.04000(17)	0.24921(12)	0.0484(7)
C3	0.5928(2)	1.03149(19)	0.21806(13)	0.0556(8)
H3	0.5864	1.0140	0.1844	0.067*
C4	0.6744(2)	1.0487(2)	0.23647(14)	0.0577(8)
H4A	0.7223	1.0443	0.2149	0.069*
C5	0.6852(2)	1.07219(18)	0.28651(14)	0.0557(8)
H5	0.7407	1.0818	0.2989	0.067*
C6	0.6138(2)	1.08206(17)	0.31940(13)	0.0493(7)
C7	0.6293(2)	1.10263(19)	0.37564(14)	0.0622(9)
H7A	0.6726	1.1427	0.3777	0.075*
H7B	0.5761	1.1222	0.3905	0.075*
C8	0.6592(2)	1.03458(19)	0.40615(12)	0.0529(7)
C9	0.7474(2)	1.0196(2)	0.41321(13)	0.0632(9)
H9	0.7881	1.0538	0.4002	0.076*
C10	0.7752(2)	0.9551(2)	0.43918(14)	0.0662(10)
H10	0.8341	0.9462	0.4437	0.079*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C11	0.7158(2)	0.9041(2)	0.45837(13)	0.0620(9)
H11	0.7352	0.8607	0.4756	0.074*
C12	0.6268(2)	0.9158(2)	0.45272(12)	0.0533(7)
C13	0.5995(2)	0.98151(19)	0.42665(12)	0.0505(7)
C14	0.5622(2)	0.8582(2)	0.47303(13)	0.0607(8)
H14A	0.5111	0.8850	0.4853	0.073*
H14B	0.5874	0.8310	0.5020	0.073*
C15	0.5360(2)	0.80123(19)	0.43190(13)	0.0540(8)
C16	0.5915(2)	0.7417(2)	0.41828(15)	0.0676(10)
H16	0.6428	0.7350	0.4365	0.081*
C17	0.5720(3)	0.6928(2)	0.37869(17)	0.0736(11)
H17	0.6089	0.6522	0.3713	0.088*
C18	0.4983(2)	0.70339(19)	0.34972(15)	0.0639(9)
H18	0.4871	0.6711	0.3220	0.077*
C19	0.43994(19)	0.76204(17)	0.36149(13)	0.0511(7)
C20	0.45978(19)	0.80813(16)	0.40398(12)	0.0464(7)
C21	0.3614(2)	0.77487(19)	0.32779(13)	0.0570(8)
H21A	0.3346	0.7258	0.3205	0.068*
H21B	0.3197	0.8057	0.3466	0.068*
C22	0.38191(18)	0.81403(18)	0.27750(12)	0.0506(7)
C23	0.3839(2)	0.7740(2)	0.23143(16)	0.0686(10)
H23	0.3724	0.7217	0.2316	0.082*
C24	0.4025(2)	0.8096(3)	0.18558(15)	0.0726(11)
H24	0.4041	0.7814	0.1551	0.087*
C25	0.4189(2)	0.8879(2)	0.18478(14)	0.0645(9)
H25	0.4313	0.9119	0.1536	0.077*
C26	0.41713(18)	0.93040(19)	0.22966(12)	0.0511(7)
C27	0.39856(17)	0.89297(17)	0.27589(12)	0.0454(7)
C28	0.4314(2)	1.01632(19)	0.22848(14)	0.0575(8)
H28A	0.3868	1.0410	0.2489	0.069*
H28B	0.4257	1.0343	0.1932	0.069*
C29	0.4127(2)	1.14773(19)	0.32570(16)	0.0661(10)
H29A	0.4148	1.1655	0.2902	0.079*
H29B	0.4381	1.1868	0.3476	0.079*
C30	0.3208(2)	1.1331(2)	0.34143(16)	0.0683(10)
H30A	0.2945	1.0969	0.3178	0.082*
H30B	0.2881	1.1804	0.3400	0.082*
C31	0.2064(2)	1.0823(3)	0.41640(14)	0.0649(9)
C32	0.1661(2)	1.0144(2)	0.42095(13)	0.0608(9)
C33	0.0468(2)	1.1158(3)	0.44374(14)	0.0745(12)
C34	0.2769(2)	0.9074(2)	0.46489(13)	0.0633(9)
H34A	0.3094	0.9534	0.4729	0.076*
H34B	0.2400	0.8957	0.4941	0.076*
C35	0.3385(2)	0.8419(2)	0.45553(14)	0.0604(9)
H35A	0.3675	0.8281	0.4874	0.072*
H35B	0.3069	0.7975	0.4431	0.072*
C36	0.8656(3)	0.6406(3)	0.2943(2)	0.0944(15)
H36A	0.8909	0.5898	0.2962	0.113*
H36B	0.8965	0.6732	0.3184	0.113*

Experimental details

In the crystal structure, all hydrogen atoms were positioned geometrically and refined using a riding model. Methyl C—H bonds were fixed at 0.97 Å with $U_{iso}(H) = 1.5U_{eq}(C)$. Aromatic C—H distances were set to 0.93 Å and O—H set to 0.82 Å with $U_{iso}(H)$ set to $1.2U_{eq}$ for the parent atoms.

Comment

Calixarene-tetrathiafulvalene derivatives have found a widespread use in molecular recognition, as molecular devices and electron transfer area [7]. As an intermediate of calixarene-tetrathiafulvalene, the synthesis of the title compound is important for us.

The title structure contains one 25,27-(2,2′-[(2-thioxo-1,3-dithiole-4,5-diyl)disulfanediyl]diethanolate)-26,28-dihydroxycalix[4]arene and one dichloromethane molecule. As shown in the figure, the calixarene skeleton adopts a cone conformation. The molecular conformation is stabilized by two intramolecular hydrogen bond (O2—H2···O3 (d(H2···O3) = 2.08 Å) and O4—H4···O1 (d(H4···O1) = 1.97 Å).

All molecular geometric parameters are in the expected ranges [8].

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