metal-organic compounds

trans-Bis(1,2-dimethoxyethane-κ^2O,O')-diiodido(tetrahydrofuran-κO)calcium(II)

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In the title compound, $[CaI_2(C_4H_8O)(C_4H_{10}O_2)_2]$, the Ca atom is situated in the centre of a distorted pentagonal bipyramid. Two iodide anions occupy the axial positions, whereas the five oxygen donor atoms of two molecules of 1,2-dimethoxyethane and one molecule of tetrahydrofuran occupy the equatorial positions. The molecule is located on a crystallographic C_2 axis.

Related literature

For literature on the synthesis and structural characterization of calcium diiodide complexes with ether ligands, see: Tesh *et al.* (1994) and Henderson *et al.* (2005) for (thf)$_4$CaI$_2$ (thf = tetrahydrofuran); Fromm (2002) for (dme)(diglyme)CaI$_2$ (dme = 1,2-dimethoxyethane, diglyme = diglycoldimethyl ether); Fromm & Maudez (2003) for (dme)$_3$CaI(I) and (diglyme)$_2$CaI(I). For literature on crown ether complexes of the heavy alkaline earth metal halides, see: Junk & Steed (2007). See Fromm, Goesmann *et al.* (2000); Fromm, Bernardinelli *et al.* (2000); Fromm (2001) for calcium diiodide complexes with hydroxo and ether ligands. For related literature, see: Gärtner *et al.* (2007).
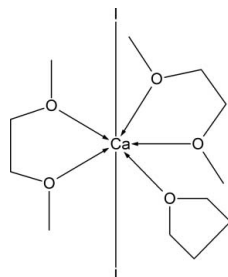
Experimental

Crystal data

$[CaI_2(C_4H_8O)(C_4H_{10}O_2)_2]$	$V = 2011.44\ (12)$ Å^3
$M_r = 546.22$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 12.8976\ (4)$ Å	$\mu = 3.39$ mm^{-1}
$b = 11.2682\ (4)$ Å	$T = 183\ (2)$ K
$c = 15.2359\ (5)$ Å	$0.04 \times 0.04 \times 0.03$ mm
$\beta = 114.715\ (2)°$	

Data collection

Nonius KappaCCD diffractometer	2279 independent reflections
Absorption correction: none	1892 reflections with $I > 2\sigma(I)$
6625 measured reflections	$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	94 parameters
$wR(F^2) = 0.069$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
2279 reflections	$\Delta\rho_{min} = -0.94$ e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

trans-Bis(1,2-dimethoxyethane-*κ²O,O'*)diiodido(tetrahydrofuran-*κO*)calcium(II)

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Comment

There are only a few molecular structures of calcium diiodides with ether ligands in literature. At first, Tesh *et al.* (1994) and Henderson *et al.* (2005) investigated the structure of $(thf)_4CaI_2$, which was used for metathesis reactions with potassium compounds (*e.g.* potassium cyclopentadienides). Later, Fromm and coworkers were able to charaterize calcium iodides with 1,2-dimethoxyethane (dme) and diglycoldimethylether (diglyme) as ligands such as $(dme)(diglyme)CaI_2$ (diglyme = diglycoldimethylether) (Fromm, 2002), $(dme)_3CaI(I)$ (Fromm & Maudez, 2003), and $(diglyme)_2CaI(I)$ (Fromm & Maudez, 2003). Single crystals of the later compound were difficult to grow, so a molecular structure does not exist. Junk & Steed (2007) prepared the 15-crown-5 or 18-crown-6 complexes of the heavy alkaline earth metal chlorides, bromides, iodides, and perchlorates and determined their molecular structures. The presence of water leads to the formation of polymers *via* hydrogen bridges (Fromm, 2001, Fromm, Goesmann *et al.*, 2000), Fromm, Bernardinelli *et al.*, 2000).

Experimental

All manipulations were carried out in an atmosphere of argon using standard Schlenk techniques. DME was dried (Na/benzophenone) and distilled prior to use. 1-Naphthylcalcium(thf)₄ iodide was prepared according to a literature procedure (Gärtner *et al.* (2007)). Recrystallization of 1-naphthylcalcium(thf)₄ iodide from 1,2-dimethoxyethane led to the formation of single crystals of the title compound at −25 °C due to a Schlenk equilibrium. The yield is approx. 50%. Bis(1-naphthyl)calcium remained in solution.

Refinement

All hydrogen atoms were set to idealized positions and were refined with 1.2 times (1.5 for methyl groups) the isotropic displacement parameter of the corresponding carbon atom. The methyl groups were allowed to rotate but not to tip.

Figures
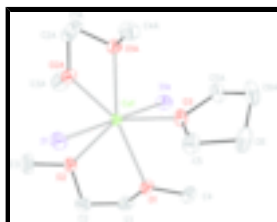

Fig. 1. The molecular structure of $(thf)(dme)_2CaI_2$, showing 40% probability displacement ellipsoides and the atom-numbering scheme. H atoms have been omitted for clarity. Symmetry operator (A): $1 - x, y, 3/2 - z$.

supplementary materials

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Crystal data

$[CaI_2(C_4H_8O)(C_4H_{10}O_2)_2]$	$F_{000} = 1064$
$M_r = 546.22$	$D_x = 1.804$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C2yc	Cell parameters from 6625 reflections
$a = 12.8976$ (4) Å	$\theta = 2.5$–27.5º
$b = 11.2682$ (4) Å	$\mu = 3.39$ mm^{-1}
$c = 15.2359$ (5) Å	$T = 183$ (2) K
$\beta = 114.715$ (2)º	Prism, colourless
$V = 2011.44$ (12) Å^3	$0.04 \times 0.04 \times 0.03$ mm
$Z = 4$	

Data collection

KappaCCD diffractometer	1892 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.020$
Monochromator: graphite	$\theta_{max} = 27.5$º
$T = 183(2)$ K	$\theta_{min} = 2.5$º
φ and ω scan	$h = -16 \rightarrow 16$
Absorption correction: none	$k = -14 \rightarrow 14$
6625 measured reflections	$l = -16 \rightarrow 19$
2279 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.069$	$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 3.2686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.002$
2279 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
94 parameters	$\Delta\rho_{min} = -0.94$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Ca1	0.5000	0.24628 (5)	0.7500	0.02044 (15)
I1	0.582761 (14)	0.248498 (14)	0.583681 (11)	0.03409 (9)
O1	0.29341 (13)	0.29633 (16)	0.65423 (12)	0.0271 (3)
O2	0.38695 (14)	0.07448 (15)	0.66082 (13)	0.0311 (4)
O3	0.5000	0.45785 (19)	0.7500	0.0277 (5)
C1	0.2241 (2)	0.1915 (2)	0.63757 (19)	0.0326 (5)
H1A	0.1443	0.2097	0.5928	0.039*
H1B	0.2248	0.1629	0.6992	0.039*
C2	0.2712 (2)	0.0987 (2)	0.59491 (18)	0.0338 (5)
H2A	0.2250	0.0254	0.5831	0.041*
H2B	0.2686	0.1266	0.5324	0.041*
C3	0.4316 (3)	−0.0220 (3)	0.6253 (3)	0.0512 (8)
H3A	0.3846	−0.0929	0.6180	0.077*
H3B	0.5103	−0.0385	0.6712	0.077*
H3C	0.4302	−0.0004	0.5625	0.077*
C4	0.2358 (2)	0.3955 (2)	0.6731 (2)	0.0379 (6)
H4A	0.1612	0.4062	0.6187	0.057*
H4B	0.2817	0.4674	0.6812	0.057*
H4C	0.2253	0.3807	0.7322	0.057*
C5	0.4803 (3)	0.5323 (2)	0.6664 (2)	0.0365 (6)
H5A	0.4118	0.5056	0.6097	0.044*
H5B	0.5468	0.5298	0.6499	0.044*
C6	0.4632 (3)	0.6564 (2)	0.6962 (2)	0.0451 (7)
H6A	0.4891	0.7172	0.6629	0.054*
H6B	0.3821	0.6710	0.6822	0.054*

Atomic displacement parameters ($\mathring{A}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0186 (3)	0.0192 (3)	0.0237 (3)	0.000	0.0090 (3)	0.000
I1	0.03470 (13)	0.04437 (14)	0.02571 (13)	0.00171 (7)	0.01510 (9)	−0.00373 (6)
O1	0.0209 (8)	0.0271 (8)	0.0335 (9)	0.0033 (7)	0.0116 (7)	0.0011 (7)
O2	0.0280 (9)	0.0247 (8)	0.0379 (9)	−0.0004 (7)	0.0112 (7)	−0.0074 (7)
O3	0.0344 (12)	0.0197 (11)	0.0325 (12)	0.000	0.0173 (10)	0.000
C1	0.0200 (11)	0.0365 (14)	0.0373 (13)	−0.0038 (10)	0.0082 (10)	0.0023 (11)
C2	0.0308 (12)	0.0327 (13)	0.0304 (12)	−0.0061 (10)	0.0053 (10)	−0.0035 (10)
C3	0.0524 (18)	0.0313 (14)	0.072 (2)	0.0023 (13)	0.0276 (16)	−0.0161 (14)

C4	0.0312 (13)	0.0371 (14)	0.0457 (15)	0.0115 (11)	0.0163 (12)	0.0003 (12)
C5	0.0474 (15)	0.0290 (13)	0.0384 (14)	0.0019 (11)	0.0233 (12)	0.0059 (11)
C6	0.0598 (18)	0.0246 (12)	0.0659 (18)	0.0087 (12)	0.0411 (16)	0.0116 (12)

Geometric parameters (Å, °)

Ca1—O3	2.384 (2)	C1—H1B	0.9900
Ca1—O2^i	2.4624 (17)	C2—H2A	0.9900
Ca1—O2	2.4624 (17)	C2—H2B	0.9900
Ca1—O1	2.5092 (16)	C3—H3A	0.9800
Ca1—O1^i	2.5092 (16)	C3—H3B	0.9800
Ca1—I1	3.13418 (18)	C3—H3C	0.9800
Ca1—I1^i	3.13419 (18)	C4—H4A	0.9800
O1—C4	1.436 (3)	C4—H4B	0.9800
O1—C1	1.438 (3)	C4—H4C	0.9800
O2—C2	1.434 (3)	C5—C6	1.515 (4)
O2—C3	1.438 (3)	C5—H5A	0.9900
O3—C5	1.456 (3)	C5—H5B	0.9900
O3—C5^i	1.456 (3)	C6—C6^i	1.512 (6)
C1—C2	1.488 (4)	C6—H6A	0.9900
C1—H1A	0.9900	C6—H6B	0.9900
O3—Ca1—O2^i	141.83 (4)	O1—C1—H1B	110.0
O3—Ca1—O2	141.83 (4)	C2—C1—H1B	110.0
O2^i—Ca1—O2	76.34 (8)	H1A—C1—H1B	108.4
O3—Ca1—O1	77.01 (4)	O2—C2—C1	108.85 (19)
O2^i—Ca1—O1	137.52 (6)	O2—C2—H2A	109.9
O2—Ca1—O1	67.42 (6)	C1—C2—H2A	109.9
O3—Ca1—O1^i	77.01 (4)	O2—C2—H2B	109.9
O2^i—Ca1—O1^i	67.42 (6)	C1—C2—H2B	109.9
O2—Ca1—O1^i	137.51 (6)	H2A—C2—H2B	108.3
O1—Ca1—O1^i	154.02 (8)	O2—C3—H3A	109.5
O3—Ca1—I1	89.543 (10)	O2—C3—H3B	109.5
O2^i—Ca1—I1	97.42 (4)	H3A—C3—H3B	109.5
O2—Ca1—I1	83.30 (4)	O2—C3—H3C	109.5
O1—Ca1—I1	99.55 (4)	H3A—C3—H3C	109.5
O1^i—Ca1—I1	80.24 (4)	H3B—C3—H3C	109.5
O3—Ca1—I1^i	89.543 (10)	O1—C4—H4A	109.5
O2^i—Ca1—I1^i	83.30 (4)	O1—C4—H4B	109.5
O2—Ca1—I1^i	97.42 (4)	H4A—C4—H4B	109.5
O1—Ca1—I1^i	80.24 (4)	O1—C4—H4C	109.5
O1^i—Ca1—I1^i	99.55 (4)	H4A—C4—H4C	109.5
I1—Ca1—I1^i	179.09 (2)	H4B—C4—H4C	109.5
C4—O1—C1	109.85 (19)	O3—C5—C6	105.3 (2)
C4—O1—Ca1	124.81 (14)	O3—C5—H5A	110.7
C1—O1—Ca1	110.38 (14)	C6—C5—H5A	110.7

C2—O2—C3	110.1 (2)	O3—C5—H5B	110.7
C2—O2—Ca1	116.08 (14)	C6—C5—H5B	110.7
C3—O2—Ca1	124.35 (16)	H5A—C5—H5B	108.8
C5—O3—C5^i	109.6 (3)	C6^i—C6—C5	102.74 (19)
C5—O3—Ca1	125.19 (13)	C6^i—C6—H6A	111.2
C5^i—O3—Ca1	125.19 (13)	C5—C6—H6A	111.2
O1—C1—C2	108.5 (2)	C6^i—C6—H6B	111.2
O1—C1—H1A	110.0	C5—C6—H6B	111.2
C2—C1—H1A	110.0	H6A—C6—H6B	109.1

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2.

Fig. 1