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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.018 \text{ \AA}$
Disorder in main residue
R factor = 0.058
wR factor = 0.171
Data-to-parameter ratio = 18.7

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

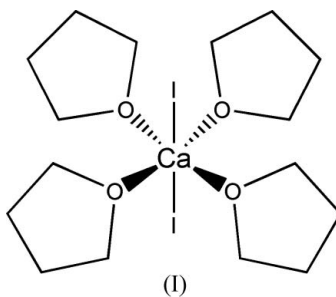
A low-temperature investigation of *trans*-diiodo-
tetrakis(tetrahydrofuran)calcium(II)

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The asymmetric unit of the title compound, $[\text{CaI}_2(\text{C}_4\text{H}_8\text{O})_4]$, at 100 K comprises half each of two independent molecules, each of which is located on a center of inversion, and in each of these, the central Ca atom is bound by two *trans* I atoms and four tetrahydrofuran molecules to give a distorted octahedral geometry. This compound undergoes a phase change on cooling from room temperature to 100 K, altering the space group from monoclinic $P2_1/c$ to triclinic $P\bar{1}$. This change is also accompanied by a reduction in the positional disorder of the coordinated tetrahydrofuran molecules.

Comment

As part of our ongoing investigations into the chemistry of the alkaline earth metals (He *et al.*, 2005), we crystallized the title compound, (I). The room-temperature structure of (I) was first reported by Tesh *et al.* (1994). The original experiment found the monoclinic space group $P2_1/c$ with unit-cell parameters $a = 8.201(7)$, $b = 14.262(9)$, $c = 10.008(6) \text{ \AA}$, $\beta = 93.93(6)^\circ$ and $Z = 2$. The asymmetric unit comprised a half-molecule, with the Ca atom on an inversion center. Disorder was indicated in the atomic positions of the attached tetrahydrofuran (THF) molecules, as the molecules appear almost planar. We confirmed the identity of the room-temperature unit cell, but found that cooling to 100 K resulted in a phase change to the triclinic space group $P\bar{1}$ with unit-cell parameters as listed in the *Crystal data* section. This phase change proved to be reversible upon warming the crystal to room temperature. The low-temperature structure was refined as a four-component non-merohedral twin. Twin domains were identified using *CELL_NOW* (Sheldrick, 2005). The scale factors for the four components are 0.412(2), 0.331(2), 0.136(2) and 0.121(2).



Two independent half-molecules with similar metrical parameters constitute the asymmetric unit; the molecules are shown in Fig. 1. One molecule has a pair of well defined THF ligands and a pair of easily modeled two-site disordered THF ligands. The other exhibits no disorder. Overlaying one half-

molecule on the other shows differences principally in the angles between the attached *cis* ligands. One of the molecules has these angles in the narrow range 88.55 (19)–91.45 (19)°, whereas these angles in the second molecule are in the range 84.36 (3)–95.65 (3)°. The analogous angles in the room-temperature structure are in the range 89.06 (6)–90.94 (7)°.

Experimental

All experimental manipulations were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. Hexane and THF were dried using a solvent purification system and stored over 4 Å molecular sieves prior to use. CaI₂ was purchased from Aldrich as anhydrous beads and used as received. The NMR data were obtained on a Varian Unity Plus 300 spectrometer at 298 K. X-ray quality crystals of (I) formed at 253 K as a by-product in the reaction of *t*BuLi (15 mmol) with CaI₂ (15 mmol) in a hexane/THF solution (3:2 *v/v*, 25 ml). ¹H NMR (300 MHz, DMSO-*d*₆, 298 K): δ 3.59 (*m*, OCH₂, THF), 1.76 (*m*, CH₂, THF).

Crystal data

[CaI ₂ (C ₈ H ₁₆ O ₂) ₂]	<i>Z</i> = 2
<i>M_r</i> = 582.30	<i>D_x</i> = 1.734 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.442 (2) Å	Cell parameters from 5033 reflections
<i>b</i> = 9.858 (2) Å	θ = 2.8–26.3°
<i>c</i> = 13.610 (3) Å	μ = 3.06 mm ⁻¹
α = 80.156 (1)°	<i>T</i> = 100 (2) K
β = 89.412 (1)°	Cut needle, colorless
γ = 87.877 (1)°	0.28 × 0.17 × 0.15 mm
<i>V</i> = 1115.2 (4) Å ³	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4361 independent reflections
φ and ω scans	3852 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (Blessing, 1995)	<i>R</i> _{int} = 0.053
<i>T</i> _{min} = 0.53, <i>T</i> _{max} = 0.64	θ _{max} = 27.0°
15968 measured reflections	<i>h</i> = -10 → 10
	<i>k</i> = -11 → 12
	<i>l</i> = -17 → 15

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.1062P)^2 + 6.8251P]$
$R[F^2 > 2\sigma(F^2)] = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.171$	(Δ/σ) _{max} = 0.002
<i>S</i> = 1.05	$\Delta\rho$ _{max} = 2.27 e Å ⁻³
4361 reflections	$\Delta\rho$ _{min} = -1.30 e Å ⁻³
233 parameters	
H-atom parameters constrained	

H atoms were placed at calculated positions and allowed to ride on the parent C atoms, with C–H set at 0.97 Å and with *U*_{iso}(H) =

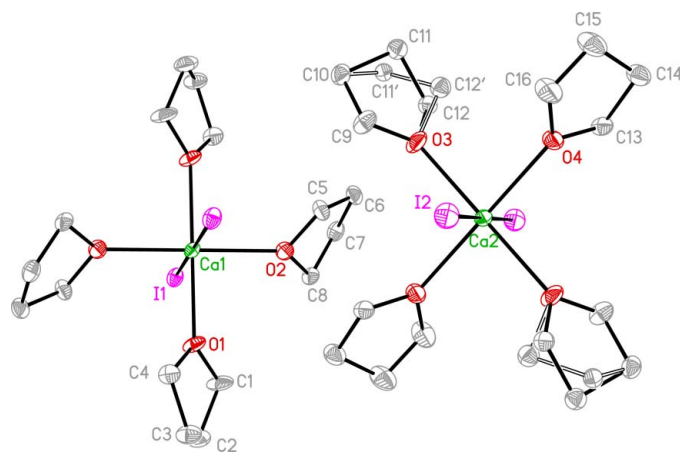


Figure 1

The structure and atomic numbering for one independent molecule in (I); the Ca atom is located on a center of inversion. Displacement ellipsoids are drawn at the 50% displacement level and H atoms have been omitted for clarity.

$1.2U_{iso}(C)$. Disorder was modeled for the O3 THF molecule in the second independent molecule so that atoms C11 and C12 were split over two sites. Anisotropic refinement of these showed that the major component has a site-occupancy factor of 0.63 (4). The four largest residual peaks in the final difference map, 2.27 to 1.34 e Å⁻³, were located near the I-atom positions, approximately perpendicular to the Ca–I bond, and may be alternate sites for these atoms. The deepest residual hole is located 0.71 Å from atom I2.

Data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: APEX2 and SAINT (Bruker–Nonius, 2004); data reduction: SAINT and SHELXTL (Sheldrick, 2004); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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