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ansa-Calcocenes: *rac*-[bis(3,3′-biacenaphthylenido)]-bis(tetrahydrofuran)calcium

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The title compound, *rac*-[Ca($C_{24}H_{12}$)(C_4H_8O)$_2$], was synthesized using activated calcium and the neutral ligand in the presence of THF. Both enantiomers are present in the asymmetric unit. The Ca atom is in a distorted pseudo-tetrahedral four-coordinate environment with the following range of bond distances and angles (*Cp* = cyclopentadienyl centroid): *Cp*—Ca 2.347 (4)–2.446 (4) Å, Ca—O 2.346 (4)–2.357 (4) Å, *Cp*—Ca—*Cp* 118.8 (2)–119.1 (2)° and O—Ca—O 87.39 (14)–87.93 (13)°.

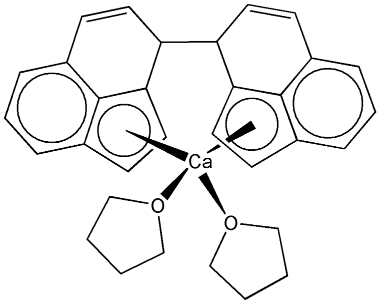
Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.008 Å
R factor = 0.054
wR factor = 0.128
Data-to-parameter ratio = 13.4

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

Comment

We have continued our studies on the synthesis of ansa-calcocenes as useful reagents for ligand transfer reactions, and have synthesized and structurally characterized the title *rac*-(acenaphthylenide)$_2$Ca(thf)$_2$ complex, (I). This complex is synthesized by coupling the neutral ligand with $HgCl_2$ activated calcium in the presence of THF. A similar synthesis was recently described in the literature (Fedushkin, Petovskaya *et al.*, 2001).



(I)

Complex (I) crystallizes in the orthorhombic system $Pca2_1$ with two independent molecules in the asymmetric unit. The coupling induced by the actived calcium exclusively yields the C_2-symmetric *rac*-ansa complex, and both enantiomers are present and are shown in Fig. 1. The calcium center is η^5-bonded to both cyclopentadienyl (Cp) moieties of the biacenaphthylenide framework and η^1 to both tetrahydrofuran molecules, resulting in a distorted pseudo-tetrahedral enviroment and a four-coordinate calcium. Most of the geometrical features of both enantiomers (identified by the central Ca atom) are essentially identical (*Cp* = cyclopentadienyl centroid): Ca—*Cp* [Ca1: 2.347 (4) and 2.446 (4) Å; Ca2: 2.446 (4) and 2.438 (4) Å]; Ca—O distances [Ca1: 2.346 (4) and 2.354 (4) Å; Ca2: 2.357 (4) and 2.351 (4) Å]; *Cp*—Ca—*Cp* angles [Ca1: 119.1 (2); Ca2: 118.8 (2)]; O—Ca—O angles [Ca1: 87.93 (13); Ca2: 87.39 (14)]. The dihedral angles between the

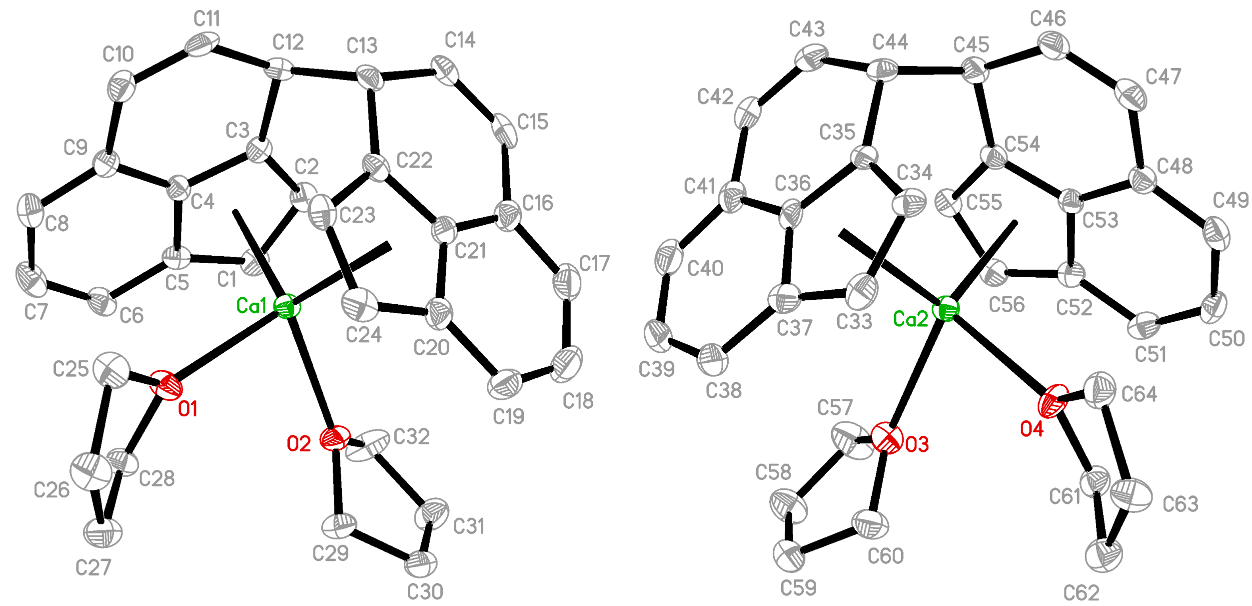


Figure 1

The molecular structure of both enantiomers in (I) with 30% probability ellipsoids. H atoms have been omitted for clarity. η^5-Bonding is represented by a solid bond from the Cp centroid to the metal. In order to show both enantiomers clearly, the relative position of each molecule in the asymmetric unit has not been maintained.

acene rings in (I) are 62.49 (7) (Ca1) and 61.50 (7)° (Ca2).

Complex (I) displays many similarities with the few structurally characterized ansa-calcocenes in general. These main structural features are given in Table 1 for the following complexes: $Me_4C_2(\eta^5\text{-}C_5H_4)_2Ca\{(CH_3)_3CN(CH)_2NC(CH_3)_3\}$, (II) (Reickhoff *et al.*, 1993), *cis*- and *trans*-$Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(thf)_2$, (III) and (IV) (Matare *et al.*, 1998; Kane *et al.*, 1997), *trans*-$Ph_2C_2H_2$-*rac*-$(\eta^5\text{-}4,7\text{-}Me_2C_9H_4)_2Ca(thf)_2$, (V) (Shapiro *et al.*, 1999), and *trans*-$Ph_2(CH_3)_2C_2(\eta^5\text{-}C_5H_4)_2Ca(DME)$, (VI) (Twamley *et al.*, 2001).

The fused acene unit has also been observed in the lanthanide complexes *rac*-$(C_{12}H_6)_2Ln(C_4H_8O)_2$ (Ln = Yb, Sm; Fedushkin, Dechert & Schumann, 2001). These complexes are isostructural with (I) and show similar geometry [acene dihedral angles: 63.9 and 62.7° (Yb); 63.6° (Sm)]. The fusion C—C bond distance in the lanthanide complexes [1.556 (4) and 1.573 (4) Å (Yb), and 1.568 (3) Å (Sm)] is similar to that in (I) [1.586 (7) and 1.559 (7) Å].

Experimental

The title compound, (I), was synthesized by combining acenaphthylene (4.60 g, 75% pure by ^{1}H NMR, 22.7 mmol) and activated calcium (2.1 g, 52 mmol); THF (150 ml) was condensed into the vessel. The clear yellow solution with calcium on the bottom turned into a brown turbid mixture after stirring overnight at room temperature. The product was extracted with hot THF until the extract became colorless. The raw product was washed twice with benzene (2 × 50 ml) and dried under reduced pressure. Isolation gave 5.05 g (10.33 mmol, 91%) of a green–yellow product. The ^{1}H NMR spectrum showed one isomer (rac) was present. Crystals suitable for X-ray analysis were obtained by slow cooling of a hot saturated THF solution of the title compound. ^{1}H NMR (500.13 MHz, THF-d_8): δ 6.87 (*d*, $^1J_{HH}$ = 8.25 Hz, 2H, H-5), 6.60 (*dd*, $^3J_{HH}$ = 9.68 Hz, $^4J_{HH}$ = 1.93 Hz, 2H, H-6), 6.40 (*dd*, $^3J_{HH}$ = 8.25 Hz, $^3J_{HH}$ = 6.50 Hz, 2H, H-4), 6.33 (*d*, $^3J_{HH}$ = 3.14 Hz, 2H, H-2), 6.22 (*d*, $^3J_{HH}$ = 6.50 Hz, 2H, H-3), 5.99 (*dd*, $^3J_{HH}$ = 9.68 Hz, $^3J_{HH}$ = 3.53 Hz, 2H, H-7), 5.59 (*d*, 3 J_{HH} = 3.14 Hz, 2H, H-1), 4.54 (*br*, 2H, H-8); 3.58 (*m*, 8H, THF), 1.73 (*m*, 8H, THF). ^{13}C NMR (125.77 MHz, THF-d_8): δ 135.56 (*d*, $^1J_{CH}$ = 157.7 Hz), 128.61 (*s*), 127.24 ($^1J_{CH}$ = 155.5 Hz), 124.22 (*s*), 120.70 (*d*, $^1J_{CH}$ = 154.3 Hz), 119.00 (*d*, $^1J_{CH}$ = 154.5 Hz), 113.52 (*d*, $^1J_{CH}$ = 159.0 Hz), 112.68 (*d*, $^1J_{CH}$ = 151.5 Hz), 112.14 (*s*), 96.18 (*d*, $^1J_{CH}$ = 163.0 Hz), 67.4 (*m*, THF), 50.00 (*d*, $^1J_{CH}$ = 130.7 Hz, C-8), 25.32 (*m*, THF).

Crystal data

$[Ca(C_{24}H_{12})(C_4H_8O)_2]$
M_r = 488.66
Orthorhombic, $Pca2_1$
a = 16.1497 (14) Å
b = 8.6805 (7) Å
c = 35.047 (3) Å
V = 4913.2 (7) Å^3
Z = 8
D_x = 1.321 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 928 reflections
θ = 2.3–22.5°
μ = 0.28 mm^{-1}
T = 203 (2) K
Plate, yellow
0.24 × 0.14 × 0.05 mm

Data collection

Siemens SMART 1K diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1999)
T_{min} = 0.935, T_{max} = 0.986
36 582 measured reflections
8481 independent reflections

5906 reflections with $I > 2\sigma(I)$
R_{int} = 0.074
θ_{max} = 25.0°
$h = -16 \rightarrow 19$
$k = -10 \rightarrow 10$
$l = -39 \rightarrow 41$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.128
S = 1.01
8481 reflections
631 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.11 (5)

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Table 1
Selected geometrical features (Å, °) of complexes similar to (I).

Cp is the cyclopentadienyl centroid.

	(II)	(III)	(IV)	(V)	(VI)
Ca—*Cp*	2.39	2.40	2.35	2.45	2.38
Ca—O	–	2.38	2.42	2.34	2.39
Cp—Ca—*Cp*	119.1	120.4	119.9	118.6	121.3
Dihedral	61.1	61.3	63.0	66.2	59.6

Note: average values given. References: $Me_4C_2(\eta^5\text{-}C_5H_4)_2Ca\{(CH_3)_3CN(CH)_2NC(CH_3)_3\}$, (II) (Reickhoff *et al.*, 1993), *cis*- and *trans*-$Ph_2C_2H_2(\eta^5\text{-}C_5H_4)_2Ca(thf)_2$, (III) and (IV) (Matare *et al.*, 1998; Kane *et al.*, 1997), *trans*-$Ph_2C_2H_2$-*rac*-$(\eta^5\text{-}4,7\text{-}Me_2C_9H_4)_2Ca(thf)_2$, (V) (Shapiro *et al.*, 1999), and *trans*-$Ph_2(CH_3)_2C_2(\eta^5\text{-}C_5H_4)_2Ca(DME)$, (VI) (Twamley *et al.*, 2001).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT–Plus* (Bruker, 1999); program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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References

Bruker (1998). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.

Fedushkin, I. L., Dechert, S. & Schumann, H. (2001). *Angew. Chem. Int. Ed.* **40**, 561–63.

Fedushkin, I. L., Petovskaya, T. V., Bochkarev, M. N., Dechert, S. & Schumann, H. (2001). *Angew. Chem. Int. Ed.* **40**, 2474–2477.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Kane, K. M., Shapiro, P. J., Vij, A. & Cubbon, R. (1997). *Organometallics*, **16**, 4567–4571.

Matare, G. J., Kane, K. M., Shapiro, P. J. & Vij, A. (1998). *J. Chem. Crystallogr.* **28**, 731–734.

Reickhoff, M., Pieper, U., Stalke, D. & Edelmann, F. T. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 1079–1081.

Shapiro, P. J., Kane, K. M., Vij, A., Stelck, D., Matare, G. J., Hubbard, R. L. & Caron, B. (1999). *Organometallics*, **18**, 3468–3473.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1999). *SADABS*. Version 2.01. Bruker AXS Inc., Madison, Wisconsin, USA.

Twamley, B., Matare, G. J., Shapiro, P. J. & Vij, A. (2001). *Acta Cryst.* E**57**, m402–m403.

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