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A linear trinuclear $CaZn_2$ complex with bridging benzoate ligands

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Key indicators

Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.005 Å
R factor = 0.040
wR factor = 0.097
Data-to-parameter ratio = 13.1

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

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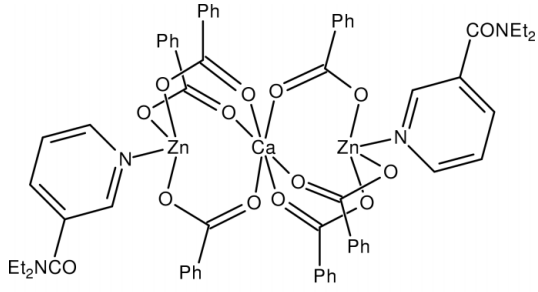
The title complex, $[CaZn_2(C_7H_5O_2)_6(C_{10}H_{14}N_2O)_2]$, has a centrosymmetric molecule containing a linear array of two zinc and one central calcium ions bridged by two sets of three unsymmetrical benzoate ligands. Zinc is additionally coordinated by a nitrogen-base ligand to give distorted tetrahedral geometry, while the coordination of calcium by six benzoate O atoms is close to regular octahedral.

Comment

The title compound, (I), was obtained as a minor product in the preparation of the bridged dimeric complex $[Zn_2(benzoate)_4(DENA)_2]$, where DENA is *N*,*N*′-diethylnicotinamide. The calcium is derived from impurities in the reagents. Crystals of (I) were separated manually from those of the major product, which has also been crystallographically characterized (Necefoglu *et al.*, 2002).



(I)

The molecule (Fig. 1) has crystallographic inversion symmetry. Six benzoate bridges link the central calcium ion with the two zinc ions, the three metal ions forming a symmetrical linear array. Each zinc ion is additionally coordinated by a monodentate DENA ligand to give somewhat distorted tetrahedral coordination by one N and three O atoms. Coordination of calcium is reasonably close to ideal octahedral (Table 1). There are no significant intermolecular interactions.

The benzoate ligands are not symmetrical. Each has one short C—O bond, which coordinates to Ca, and one longer C—O bond, coordinated to Zn; there is thus some localization of double and single bonds in the carboxylate groups. The Ca—O—C angles are considerably greater than Zn—O—C. These features are similar to those of a previously reported $CaZn_2$ complex with crotonate bridging ligands, which has been compared in detail with other MZn_2 analogous complexes having a range of transition and main-group metals *M* (Clegg *et al.*, 1988).

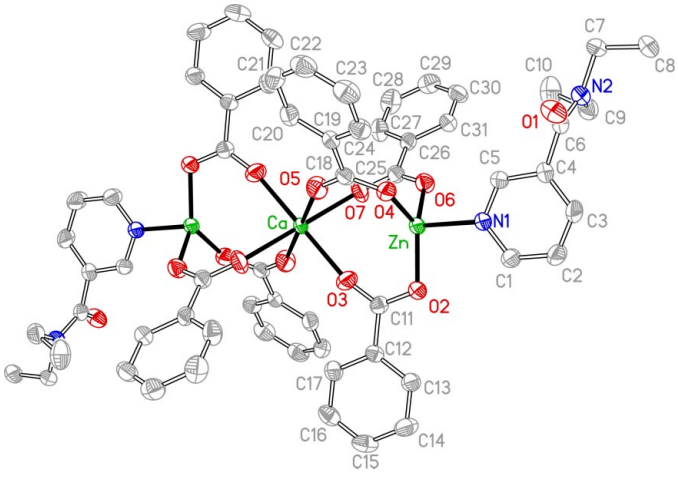


Figure 1
The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

The title complex was obtained as a minor product in the synthesis of a dimeric zinc complex with benzoate bridges (Necefolglu *et al.*, 2002). The two products could be distinguished by their different crystal habits. The minor product has its origin in the presence of calcium ions in the unpurified tap water used in the synthesis.

Crystal data

$[CaZn_2(C_7H_5O_2)_6(C_{10}H_{14}N_2O)_2]$
M_r = 1253.94
Monoclinic, $P2_1/n$
a = 16.347 (2) Å
b = 10.7691 (13) Å
c = 17.647 (2) Å
β = 107.207 (3)°
V = 2967.6 (6) Å^3
Z = 2
D_x = 1.403 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7387 reflections
θ = 2.0–25.4°
μ = 0.96 mm^{-1}
T = 160 (2) K
Block, colourless
0.30 × 0.20 × 0.16 mm

Data collection

Siemens SMART 1K CCD diffractometer
ω scans with narrow frames
Absorption correction: multi-scan (*SHELXTL*; Sheldrick, 1997)
T_{min} = 0.860, T_{max} = 0.925
12317 measured reflections
4938 independent reflections
4193 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.5°
$h = -17 \rightarrow 18$
$k = -12 \rightarrow 12$
$l = -20 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.097
S = 1.12
4938 reflections
376 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 2.7427P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N1	2.077 (2)	O2—C11	1.277 (3)
Zn—O2	1.942 (2)	O3—C11	1.242 (3)
Zn—O4	1.959 (2)	O4—C18	1.276 (3)
Zn—O6	1.943 (2)	O5—C18	1.238 (3)
Ca—O3	2.273 (2)	O6—C25	1.275 (4)
Ca—O7	2.311 (2)	O7—C25	1.243 (3)
N1—Zn—O2	96.04 (9)	O5—Ca—O7	85.49 (8)
N1—Zn—O4	95.55 (9)	Zn—O2—C11	112.66 (18)
N1—Zn—O6	97.64 (9)	Ca—O3—C11	166.6 (2)
O2—Zn—O4	126.44 (9)	Zn—O4—C18	126.02 (19)
O2—Zn—O6	125.51 (9)	Ca—O5—C18	150.7 (2)
O4—Zn—O6	104.28 (9)	Zn—O6—C25	124.59 (19)
O3—Ca—O7	88.09 (8)	Ca—O7—C25	150.8 (2)

Since this was an early experiment with one of the first commercial CCD diffractometers, operating parameters were not yet optimized. One consequence is the rather low maximum θ, as a result of a crystal-to-detector distance of approximately 6 cm. Data are essentially complete, however, to θ = 24°. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: local programs; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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