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A tetranuclear zinc–cerium complex: diaquaocta-μ-α-methylacrylato-di-α-methylacrylatodipyridinediceriumdizinc

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In the title complex, a centrosymmetric carboxylate-bridged tetranuclear zinc-cerium derivative, $[Zn_2Ce_2(C_4H_5O_2)_{10}(C_5H_5N)_2(H_2O)_2]$, the Ce^{III} and Zn^{II} ions are bridged by two bidentate carboxylato groups [Ce$\cdots$Zn 4.139 (1) Å], while the Ce ions are linked through the three bidentate carboxylate groups [Ce$\cdots$Ce 4.430 (1) Å]. The Ce atoms are nine-coordinate and the coordination polyhedron is a distorted tricapped trigonal prism. The Zn atoms are four-coordinate with a distorted tetrahedral geometry.

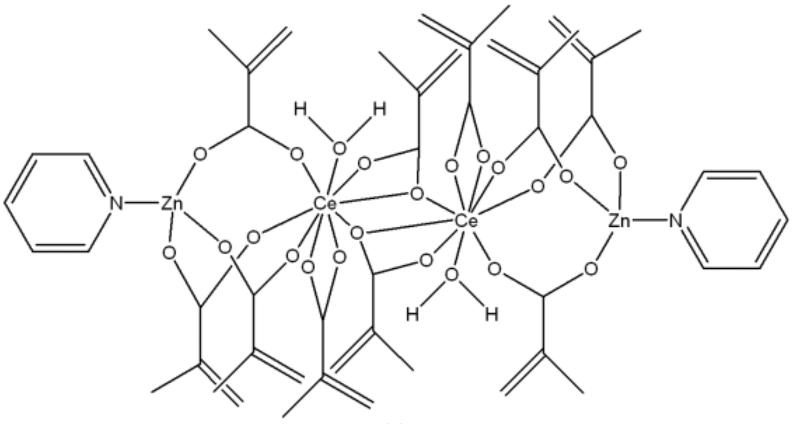
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
R factor = 0.024
wR factor = 0.056
Data-to-parameter ratio = 18.8

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

Comment

The study of heterometallic complexes containing *d*-transition metal and lanthanide(III) cations connected by bridging ligands is being actively pursued because of their relevance in solid-state technology and as models for magnetic studies (Margeat *et al.*, 2004; Wu *et al.*, 2003; Tang *et al.*, 2002). In most polynuclear compounds, the *d*-transition metal ions and lanthanide ions are bridged by multi-group ligands (Ma *et al.*, 2000; Margeat *et al.*, 2004). In this paper, we report the synthesis and crystal structure determination of the title novel complex, (I), in which the Zn^{II} and Ce^{III} cations are bridged by α-unsaturated carboxylate groups.



(I)

Complex (I) consists of a discrete tetranuclear Zn_2Ce_2 core bridged by α-methylacryl groups. The Zn and Ce ions are bridged by three carboxyl groups, while the symmetry-related Ce ions are linked by two carboxyl groups. Each Ce^{III} ion is coordinated by nine O atoms from one chelating and five bridging carboxyl groups, and from a water molecule. The nine O atoms form a distorted tricapped trigonal prism, with atoms

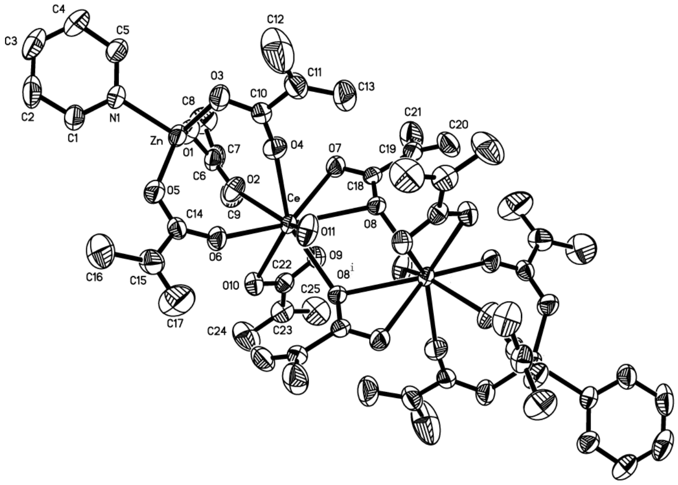


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

O2, O4, O6, O8, O8^{i} and O9 forming a trigonal prism with atoms O7, O10 and O11 as the caps [symmetry code: (i) $1-x, 1-y, 1-z$]. Each Zn^{II} ion in the complex is four-coordinated by three O atoms from three carboxyl groups and an N atom from a pyridine group. The coordination polyhedron of the Zn ion is a slightly distorted tetrahedron.

In the molecule of (I), the water molecule also forms a hydrogen bond with an O atom of the carboxyl group, with O11···O9 2.666 (3) Å.

Experimental

CeL_3·H_2O [860 mg, 2.0 mmol; HL is $CH_2C(CH_3)COOH$] and $Zn(NO_3)_2·6H_2O$ (297 mg, 1.0 mmol) were dissolved in H_2O (15 ml), and the pH was adjusted to 4.0 using HL. Pyridine solution (1.0 ml, 1 *M*) was then added. After filtration, the filtrate was allowed to stand at room temperature and single crystals of (I) suitable for X-ray analysis were obtained after two weeks. Analysis, calculated: C 41.24, H 4.43, N 1.92%; found: C 41.20, H 4.31, N 2.01%. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 1454, 1561, 1647.

Crystal data

$[Zn_2Ce_2(C_4H_5O_2)_{10}(C_5H_5N)_2(H_2O)_2]$
$M_r = 1456.05$
Triclinic, $P\overline{1}$
$a = 11.0788$ (3) Å
$b = 11.9997$ (3) Å
$c = 12.4604$ (4) Å
$\alpha = 99.3360$ (10)°
$\beta = 106.3000$ (10)°
$\gamma = 101.5560$ (10)°
$V = 1515.09$ (8) Å^3

$Z = 1$
$D_x = 1.596$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5723 reflections
$\theta = 3.0$–27.4°
$\mu = 2.33$ mm^{-1}
$T = 273$ (2) K
Prism, colourless
0.30 × 0.20 × 0.17 mm

Data collection

Rigaku RAXIS-RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.578$, $T_{max} = 0.673$
14 807 measured reflections

6882 independent reflections
6062 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.4°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.056$
$S = 1.04$
6882 reflections
366 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 0.3646P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ce—O2	2.4183 (16)	Ce—O10	2.5432 (17)
Ce—O4	2.4614 (19)	Ce—O11	2.6004 (19)
Ce—O6	2.4474 (17)	Zn—O1	1.931 (2)
Ce—O7	2.5674 (18)	Zn—O3	1.956 (2)
Ce—O8	2.6385 (15)	Zn—O5	1.9409 (19)
Ce—O8^{i}	2.5652 (15)	Zn—N1	2.0658 (19)
Ce—O9	2.5641 (17)		
O2—Ce—O4	76.57 (7)	O7—Ce—O8	49.94 (5)
O2—Ce—O6	79.16 (7)	O7—Ce—O8^{i}	110.20 (5)
O2—Ce—O7	78.35 (6)	O7—Ce—O9	70.56 (6)
O2—Ce—O8	128.29 (6)	O7—Ce—O10	115.64 (6)
O2—Ce—O8^{i}	148.86 (6)	O7—Ce—O11	114.14 (7)
O2—Ce—O9	84.03 (6)	O8—Ce—O8^{i}	66.97 (6)
O2—Ce—O10	72.22 (6)	O8—Ce—O9	79.42 (5)
O2—Ce—O11	137.89 (7)	O8—Ce—O10	125.93 (5)
O4—Ce—O6	77.73 (7)	O8—Ce—O11	75.34 (6)
O4—Ce—O7	72.93 (7)	O8^{i}—Ce—O9	71.75 (5)
O4—Ce—O8	86.82 (6)	O8^{i}—Ce—O10	77.28 (5)
O4—Ce—O8^{i}	134.43 (6)	O8^{i}—Ce—O11	67.54 (6)
O4—Ce—O9	141.34 (7)	O9—Ce—O10	50.80 (5)
O4—Ce—O10	144.57 (6)	O9—Ce—O11	137.89 (6)
O4—Ce—O11	70.14 (8)	O10—Ce—O11	126.19 (7)
O6—Ce—O7	146.35 (6)	O1—Zn—O3	115.89 (10)
O6—Ce—O8	144.42 (6)	O1—Zn—O5	124.07 (9)
O6—Ce—O8^{i}	101.99 (5)	O1—Zn—N1	98.50 (8)
O6—Ce—O9	131.09 (6)	O3—Zn—O5	112.78 (10)
O6—Ce—O10	80.30 (6)	O3—Zn—N1	101.22 (8)
O6—Ce—O11	69.32 (6)	O5—Zn—N1	97.50 (8)

Symmetry codes: (i) $1-x, 1-y, 1-z$.

All non-H atoms were initially located in a difference Fourier map. All methyl H atoms were then constrained to an ideal geometry with C—H distances of 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C—C bond. The $=CH_2$ H atoms and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were restrained in idealized positions, with O—H distances of 0.85 (1) Å and H···H distances of 1.39 (1) Å.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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