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A trinuclear zinc–cerium complex: [$CeZn_2\{CH_2C(CH_3)COO\}_6(NO_3)$-(2,2′-bipyridine)$_2$]

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Key indicators

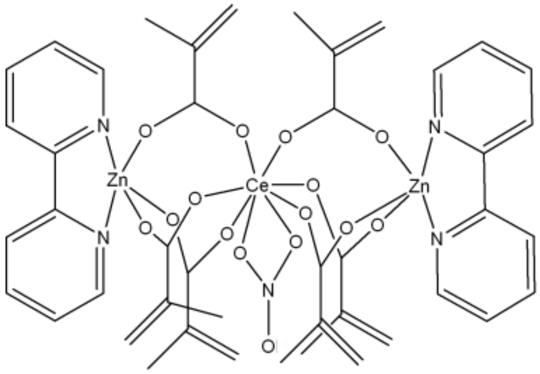
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.024
wR factor = 0.053
Data-to-parameter ratio = 14.1

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

In the novel title carboxylate-bridged trinuclear zinc–cerium complex, bis(2,2′-bipyridine)hexakis-μ-methacrylato-nitrato-cerium(III)dizinc(II), [$Zn_2Ce(C_4H_5O_2)_6(NO_3)(C_{10}H_8N_2)_2$], the Ce and each of two Zn atoms are bridged by three bidentate carboxylate groups. The Ce$\cdots$Zn separations are 4.011 (1) and 3.982 (1) Å. The Ce atom is eight-coordinate in irregular polyhedron. Each Zn atom is five-coordinate, with a distorted pyramidal geometry.

Comment

Studies on the syntheses, structures and properties of lanthanide-transition metal complexes are currently of great interest because they are good models for the investigation of the nature of the magnetic exchange interactions between 3d and 4f metal ions in magnetic materials that contain rare earth metals (Margeat *et al.*, 2004; Wu *et al.*, 2003; Zhu *et al.*, 2004). In most polynuclear compounds, the d-transition metal ions and lanthanide ions are bridged by multi-group ligands (Ma *et al.*, 2000; Liang *et al.*, 2000; Margeat *et al.*, 2004). In this paper, we report the synthesis of a new trinuclear complex in which the Zn^{II} and Ce^{III} atoms are bridged by α-unsaturated carboxylate groups.



(I)

The title complex, (I) (Fig. 1 and Table 1), contains one neutral trinuclear Zn—Ce—Zn molecule in the asymmetric unit. The Ce atom is coordinated by six O atoms from six α-methylacrylate groups and two O atoms from a nitrate group. The coordination geometry about the Ce atom is an irregular polyhedron. Each Zn atom is five-coordinated by three O atoms from three α-methylacrylate groups and two N atoms from a 2,2′-bipyridine molecule. The coordination polyhedra of atoms Zn1 and Zn2 are distorted pyramids. For Zn1, atoms N1, O1, O3 and O5 occupy the ligand sites which define the square base of the pyramid, while atom N2 occupies its apex.

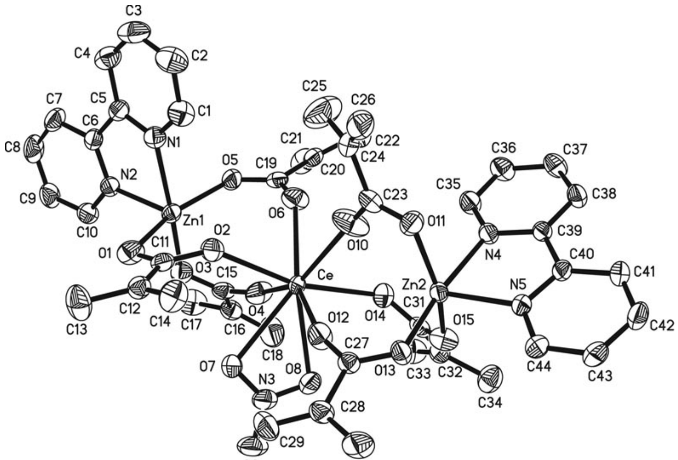


Figure 1
View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity.

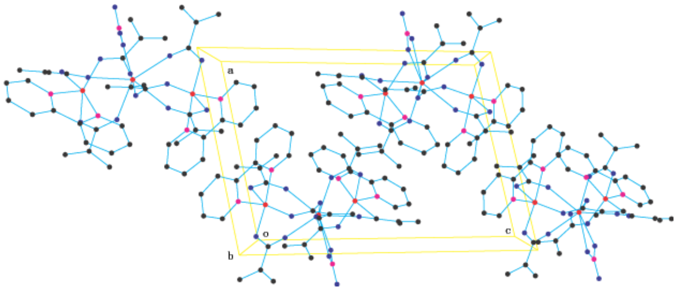


Figure 2
The molecular packing of the title compound, viewed along the b axis. Key: Ce purple, Zn green, O red, N blue and C gray. H atoms have been omitted for clarity.

For Zn2, atoms N4, O11, O13 and O15 occupy the ligand sites which define the square base of the pyramid, while atom N5 occupies its apex. The Ce and each of the two Zn atoms are bridged by three carboxylate groups. The two Ce$\cdots$Zn separations are almost equal. The Ce$\cdots$Zn1 [4.011 (1) Å] and Ce$\cdots$Zn2 separations [3.982 (1) Å] are shorter than the Ce$\cdots$Zn separation [4.139 (1) Å] in the tetranuclear complex $[ZnCe\{CH_2C(CH_3)COO\}_5(C_5H_5N)(H_2O)]_2$ (Wu & Guo, 2004).

In (I), neighboring bypiridine (bipy) ligands are anti-parallel, with an interplanar bipy–bipy distance of 3.47 Å for the bipy ligand linked with Zn1 and 3.38 Å for the bipy ligand linked with Zn2, indicating significant aromatic stacking interactions (Munakata *et al.*, 1996). The aromatic stacking interactions are responsible for the supramolecular assemblies (Fig. 2).

Experimental

$CeL_3\cdot H_2O$ [860 mg, 2.0 mmol; HL = methacrylic acid] and $Zn(NO_3)_2\cdot 6H_2O$ (445 mg, 1.5 mmol) were dissolved in 15 ml H_2O and the pH adjusted to 4.0 using HL. An ethanol solution (4 ml) of 2,2′-bipyridine (234 mg, 1.5 mmol) was added to the former solution with stirring. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray analysis were obtained after one week. Analysis calculated: C 45.72, H 4.01, N 6.06%; found: C 47.65, H 4.12, N 6.01%. Spectroscopic analysis, IR (KBr, ν cm^{-1}): 771, 833, 939, 1241, 1313, 1420, 1571, 1645.

Crystal data

$[Zn_2Ce(C_4H_5O_2)_6(NO_3)(C_{10}H_8N_2)_2]$
$M_r = 1155.76$
Triclinic, $P\overline{1}$
$a = 11.3384$ (13) Å
$b = 13.6971$ (9) Å
$c = 16.4806$ (11) Å
$\alpha = 104.434$ (1)°
$\beta = 99.374$ (1)°
$\gamma = 100.110$ (1)°
$V = 2382.2$ (4) Å^3
$Z = 2$
$D_x = 1.611$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8672 reflections
$\theta = 2.5$–$27.3°$
$\mu = 2.01$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.36 × 0.24 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.566$, $T_{max} = 0.711$
18383 measured reflections
8588 independent reflections
7565 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.5°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.053$
$S = 1.06$
8588 reflections
610 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 1.5477P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ce—O2	2.4125 (19)	Zn1—O3	2.013 (2)
Ce—O4	2.4136 (18)	Zn1—O5	2.0317 (18)
Ce—O6	2.4350 (18)	Zn1—N1	2.174 (2)
Ce—O7	2.6149 (19)	Zn1—N2	2.100 (2)
Ce—O8	2.614 (2)	Zn2—O11	2.0779 (19)
Ce—O10	2.471 (2)	Zn2—O13	2.0109 (16)
Ce—O12	2.4185 (18)	Zn2—O15	2.020 (2)
Ce—O14	2.4100 (19)	Zn2—N4	2.1877 (19)
Zn1—O1	2.0507 (18)	Zn2—N5	2.0892 (19)
O2—Ce—O4	89.12 (8)	O8—Ce—O14	71.39 (7)
O2—Ce—O6	78.29 (7)	O10—Ce—O12	72.41 (7)
O2—Ce—O7	73.88 (7)	O10—Ce—O14	78.15 (9)
O2—Ce—O8	122.72 (7)	O12—Ce—O14	92.18 (7)
O2—Ce—O10	92.17 (9)	O1—Zn1—O3	96.78 (8)
O2—Ce—O12	95.03 (7)	O1—Zn1—O5	155.68 (8)
O2—Ce—O14	165.61 (7)	O1—Zn1—N1	91.69 (8)
O4—Ce—O6	72.88 (7)	O1—Zn1—N2	99.12 (8)
O4—Ce—O7	72.89 (7)	O3—Zn1—O5	89.44 (8)
O4—Ce—O8	74.85 (7)	O3—Zn1—N1	167.88 (8)
O4—Ce—O10	143.80 (7)	O3—Zn1—N2	93.27 (8)
O4—Ce—O12	143.48 (7)	O5—Zn1—N1	86.34 (8)
O4—Ce—O14	92.48 (8)	O5—Zn1—N2	103.99 (8)
O6—Ce—O7	135.68 (6)	N1—Zn1—N2	76.78 (8)
O6—Ce—O8	140.91 (7)	O11—Zn2—O13	95.14 (7)
O6—Ce—O10	72.00 (7)	O11—Zn2—O15	156.40 (8)
O6—Ce—O12	143.46 (7)	O11—Zn2—N4	86.50 (8)
O6—Ce—O14	88.51 (7)	O11—Zn2—N5	100.54 (8)
O7—Ce—O8	48.85 (7)	O13—Zn2—O15	94.98 (8)
O7—Ce—O10	141.70 (7)	O13—Zn2—N4	172.11 (7)
O7—Ce—O12	73.52 (6)	O13—Zn2—N5	95.36 (7)
O7—Ce—O14	120.22 (7)	O15—Zn2—N4	86.38 (8)
O8—Ce—O10	131.85 (8)	O15—Zn2—N5	99.67 (9)
O8—Ce—O12	72.46 (7)	N4—Zn2—N5	76.75 (7)

All methyl H atoms were 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 $=CH_2$ and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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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