A zinc–lanthanum carboxylate complex, [LaZn₂L_6(NO₃)(bipy)₂] (L = α-methylacrylate and bipy = 2,2′-bipyridine)

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The crystal structure of the title novel heteronuclear coordination compound, tris(μ-α-methylacrylato-1:2κ^2O:O')-tris(μ-α-methylacrylato-2:3κ^2O:O')(2,2′-bipyridine-1κ^2N,N')-(2,2′-bipyridine-3κ^2N,N')(nitro-3κ^2O,O')dizinc(II)lanthanum-(III), [LaZn₂(C₄H₅O₂)₆(NO₃)(C₁₀H₈N₂)₂], is built up of discrete molecules of the trinuclear Zn–La–Zn complex, with the central La atom bridged by three bidentate α-methylacrylate groups to each of the two Zn atoms. The La atom has a distorted square-antiprismatic coordination, formed by the six O atoms of the bridging methylacrylate groups and two O atoms of the bidentate chelating nitro group. Each of the two Zn atoms has a trigonal bipyramidal coordination, formed by three O atoms of the bridging methylacrylates and two N atoms of the chelating 2,2′-bipyridine ligands.

Comment

Since the first reports of heteronuclear CuLn and NiLn complexes (Ln = lanthanide; Chisari *et al.*, 1984; Abid & Fenton, 1984), a number of heterometallic complexes involving both transition and lanthanide metals have received substantial attention, either due to their electronic, electrochemical and magnetic properties arising from the metal–metal interaction (Faser & Bosnich, 1994), or because they may be treated as models of the active centres of metalloenzymes, *e.g.* copper–zinc superoxide dismutase (Vatentine & de Freites, 1985), cytochromic oxidase (Lee & Holm, 1993) or hydrogenase (Volbeda *et al.*, 1995). To date, many polynuclear complexes containing both rare earth and transition metals have been synthesized and studied. However, data on Ln–Zn systems are relatively scarce (Liang *et al.*, 2002). In this paper, the synthesis and crystal structure of the title trinuclear LaZn₂ complex, (I), are reported.

R = CH₂C(CH₃)

(I)
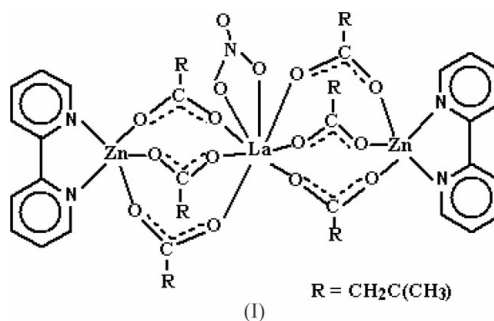
Selected bond distances and angles for (I) are listed in Table 1, and Fig. 1 shows the molecular structure.

As shown in Fig. 1, the complex contains one neutral trinuclear Zn–La–Zn molecule in the asymmetric unit. The

structure of (I) is different from the previously studied La–Zn complex [LaZnL_5(C$_2$H$_5$OH)(phen)]$_2$ (Wu *et al.*, 2002), which consists of discrete tetranuclear Zn–La–La–Zn molecules involving phenanthroline ligands. In (I), the La atom is coordinated by six O atoms from six α-methylacrylate groups and two O atoms from a nitrate ligand. The coordination geometry of the La atom may be described as distorted square antiprismatic. Each Zn atom is five-coordinated by three O atoms belonging to three α-methylacrylate groups and two N atoms of a bipy group. In the distorted trigonal bipyramidal coordination of atoms Zn1 and Zn2, atoms O10 and N1, and O14 and N4, are axial, with O10—Zn1—N1 and O14—Zn2—N4 angles of 166.85 (14) and 170.72 (12)°, respectively, whereas atoms O11, O12 and N2, and O13, O15 and N5, are in the equatorial positions.

In (I), the La^{III} and Zn^{II} atoms are bridged by three carboxylate groups in the same coordination mode of La–O–C–O–Zn. Nevertheless, the two La–Zn separations are not equal, and the La$\cdots$Zn1 distance [4.071 (4) Å] is substantially longer than La$\cdots$Zn2 [3.955 (3) Å]. The six La—O$_{carboxylate}$ bond distances show only small differences [in the range 2.429 (3)–2.507 (3) Å] and the two La—O$_{nitrate}$ distances are nearly identical [La—O1 2.636 (3) and La—O2 2.627 (3) Å]. The Zn—O bond distances range from 2.003 (3) to 2.083 (3) Å and the Zn—N bond lengths are in the range 2.095 (3)–2.185 (3) Å. All La—O, Zn—O and Zn—N bond distances are close to those observed in [LaZnL_5(C$_2$H$_5$OH)(phen)]$_2$ (Wu *et al.*, 2002).

Carboxyl groups give rise to very strong IR absorptions (Deacon & Phillips, 1980), which can be used to distinguish between the different coordination modes of the ligands (*i.e.* ionic, monodentate or bidentate) by comparison of the band separation with that of the corresponding sodium salt. The separation (146 cm^{-1}) between the antisymmetric and symmetric stretching frequencies of the OCO group in (I), being smaller than the value of 170 cm^{-1} for the sodium salt, is indicative of bidentate coordination. However, spectroscopic methods would not allow distinction between carboxylic groups with bridging bidentate and chelating bidentate coordination modes. Nevertheless, the IR spectra for (I) are consistent with the structure established by the X-ray diffraction experiment.

Experimental

LaL_3·2H$_2$O [430 mg, 1.0 mmol; HL = CH$_2$C(CH$_3$)COOH] was dissolved in water (5 ml). A solution of Zn(NO$_3$)$_2$ (1.0 ml, 1 *M*) was added and the pH was adjusted to 4.1 with 0.1 *M* HL. 2,2′-Bipyridine (156 mg, 1 mmol) was dissolved in ethanol (5 ml) and added to the mixture with stirring. After filtration, the filtrate was allowed to stand at room temperature. Single crystals of (I) suitable for X-ray analysis precipitated after two weeks. The yield, as calculated with respect to the consumed 2,2′-bipyridine, was 48.2%. The elemental analysis on C, H and N was performed using a Carlo–Erba 1110 Elemental Analyser; La and Zn were analyzed by titration with EDTA. Calculated for C$_{44}$H$_{46}$O$_{15}$N$_5$LaZn$_2$: C 45.73, H 3.98, N 6.06, La 12.03, Zn 11.33%; found: C 45.46, H 4.08, N 5.89, La 12.20, Zn 10.91%. IR spectra were recorded with a Nicolet 560 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate. IR spectra: ν_{as} (COO) 1567, ν_s (COO) 1421, ν (C=C) 1659 cm^{-1}.

Crystal data

[LaZn$_2$(C$_4$H$_5$O$_2$)$_6$(NO$_3$)-(C$_{10}$H$_8$N$_2$)$_2$]	$Z = 2$
$M_r = 1154.51$	$D_x = 1.590$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.3171$ (3) Å	Cell parameters from 8912
$b = 13.9042$ (4) Å	reflections
$c = 16.4290$ (5) Å	$\theta = 1.3$–27.5°
$\alpha = 104.360$ (1)°	$\mu = 1.93$ mm^{-1}
$\beta = 98.795$ (1)°	$T = 293$ (2) K
$\gamma = 100.214$ (2)°	Chunk, colourless
$V = 2411.6$ (1) Å^3	0.30 × 0.20 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	8229 independent reflections
ω scans	6983 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.020$
	$\theta_{max} = 25.2°$
$T_{min} = 0.599$, $T_{max} = 0.677$	$h = -12 \rightarrow 13$
13 497 measured reflections	$k = -16 \rightarrow 16$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 1.7743P]$
$wR(F^2) = 0.101$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
8229 reflections	$\Delta\rho_{max} = 1.01$ e Å^{-3}
604 parameters	$\Delta\rho_{min} = -0.95$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

La—O1	2.636 (3)	Zn1—O11	2.020 (3)
La—O2	2.627 (3)	Zn1—O12	2.025 (3)
La—O3	2.437 (3)	Zn1—N1	2.180 (4)
La—O4	2.429 (3)	Zn1—N2	2.095 (3)
La—O5	2.447 (3)	Zn2—O13	2.083 (3)
La—O6	2.461 (3)	Zn2—O14	2.003 (3)
La—O7	2.507 (3)	Zn2—O15	2.018 (4)
La—O9	2.436 (4)	Zn2—N4	2.185 (3)
Zn1—O10	2.012 (3)	Zn2—N5	2.098 (3)
O1—La—O2	48.24 (12)	O5—La—O9	97.29 (18)
O1—La—O3	72.37 (13)	O6—La—O7	72.04 (12)
O1—La—O4	74.66 (11)	O6—La—O9	87.73 (16)
O1—La—O5	72.89 (11)	O7—La—O9	79.17 (16)
O1—La—O6	135.61 (11)	O10—Zn1—O11	97.66 (15)
O1—La—O7	142.20 (13)	O10—Zn1—O12	89.52 (14)
O1—La—O9	119.58 (13)	O10—Zn1—N1	166.85 (14)
O2—La—O3	76.40 (11)	O10—Zn1—N2	92.71 (14)
O2—La—O4	122.90 (12)	O11—Zn1—O12	153.68 (14)
O2—La—O5	73.39 (13)	O11—Zn1—N1	91.78 (14)
O2—La—O6	142.15 (13)	O11—Zn1—N2	100.94 (14)
O2—La—O7	130.90 (12)	O12—Zn1—N1	85.99 (14)
O2—La—O9	71.56 (13)	O12—Zn1—N2	103.99 (13)
O3—La—O4	87.73 (13)	N1—Zn1—N2	76.45 (14)
O3—La—O5	143.91 (12)	O13—Zn2—O14	95.89 (13)
O3—La—O6	72.73 (11)	O13—Zn2—O15	155.50 (19)
O3—La—O7	143.80 (13)	O13—Zn2—N4	87.04 (13)
O3—La—O9	91.42 (18)	O13—Zn2—N5	100.84 (13)
O4—La—O5	92.34 (13)	O14—Zn2—O15	94.60 (15)
O4—La—O6	77.41 (12)	O14—Zn2—N4	170.72 (12)
O4—La—O7	92.55 (13)	O14—Zn2—N5	94.27 (12)
O4—La—O9	164.68 (14)	O15—Zn2—N4	86.13 (15)
O5—La—O6	142.27 (12)	O15—Zn2—N5	100.4 (2)
O5—La—O7	72.28 (12)	N4—Zn2—N5	76.52 (13)

All H atoms were placed in calculated positions, with C—H = 0.96 or 0.93 Å, and included in the final cycles of refinement in a riding
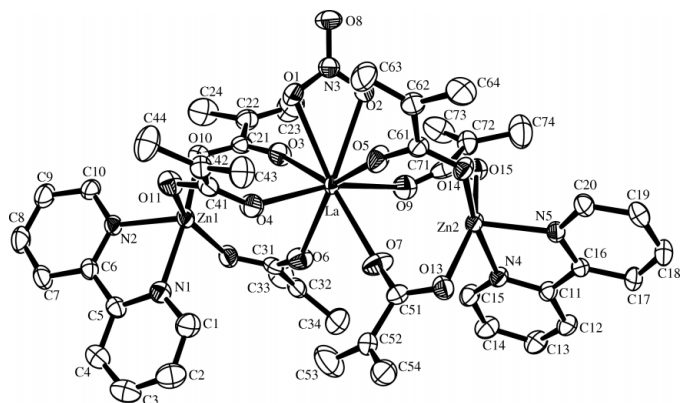
Figure 1
A view of the molecule of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms have been omitted.

model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. The maximum peak in the final difference map is 1.01 e Å^{-3} and is located in the vicinity of atoms O9, O15 and C71.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

ORTEP-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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