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Bis(2,2′-bipyridine)-1κ^2*N*:*N*′;3κ^2*N*:*N*′-tris(μ-α-methylacrylato-1:2κ^2*O*:*O*′)tris(μ-α-methylacrylato-2:3κ^2*O*:*O*′)(nitrato-2κ^2*O*:*O*′)dizinc(II)praseodymium(III)

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The crystal structure of the title heteronuclear complex, $[PrZn_2(C_4H_5O_2)_6(NO_3)(C_{10}H_8N_2)_2]$, is made up of discrete molecules of a trinuclear Zn—Pr—Zn complex with the central Pr atom bridged by three bidentate α-methylacrylate groups to each of the two Zn atoms. In the complex, the Pr atom is coordinated by six O atoms from the bridging methylacrylate groups and by two O atoms from a bidentate chelate nitrato group in a distorted square antiprismatic configuration. Each Zn ion is five-coordinated by three O atoms from three bridging methylacrylate groups and by two N atoms from a bipyridine in a distorted trigonal–bipyramidal configuration.

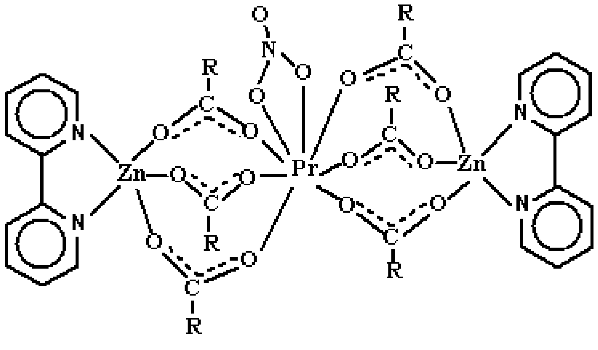
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.029
wR factor = 0.090
Data-to-parameter ratio = 14.2

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

Comment

Heteronuclear complexes involving simultaneously both transition and lanthanide metals have received much attention, either owing to their electronic, electrochemical and magnetic properties arising from metal–metal interactions (Faser & Bosnich, 1994), or being treated as the models of the active centers of some metalloenzymes, *e.g.* copper–zinc superoxide dismutase (Vatentine & Freites, 1985), cytochromic oxidase (Lee & Holm, 1993), hydrogenase (Volbeda *et al.*, 1995), *etc*. The magnetic properties of heteronuclear complexes will be affected by many factors. Interactions between metal atoms or ions including the same and different metals is one of the important factors. The present investigation of the title compound, (I), was undertaken in order to study the magnetic properties of the complex, and also as part of our molecular structure and property studies on the heteronuclear complexes of rare earth and transition metal bridged by carboxylate groups (Wu *et al.*, 2003).



$R = CH_2{=}C(CH_3)$

(I)

The title complex is isostructural with the complex $[LaZn_2\{CH_2C(CH_3)COO\}_6(NO_3)(C_{10}H_8N_2)_2]$ (Zhu *et al.*, 2004). This means that the coordination geometries about the

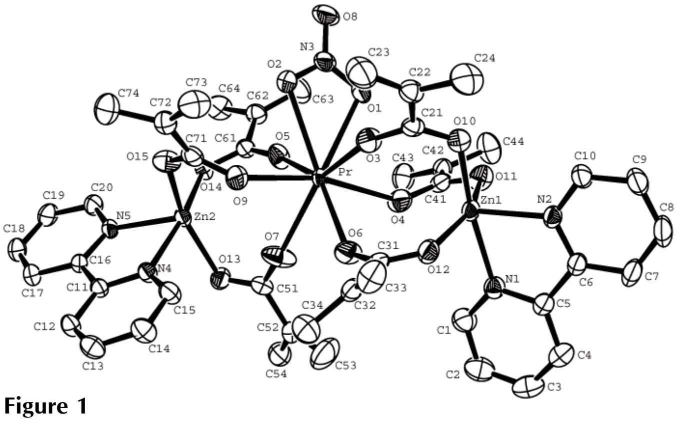


Figure 1
The molecule of the title complex, with dispalcement ellipsoids drawn at the 30% probability level

Pr and Zn atoms are the same as for the $LaZn_2$ complex and may be described as distorted square antiprismatic and trigonal–bipyramidal configurations, respectively. The Pr atom is coordinated by six O atoms from six α-methylacrylate groups and by two O atoms from a nitrate group. Each Zn ion is five-coordinated by three O atoms from three α-methylacrylate groups and by two N atoms from a bipyridine group. The title complex contains one neutral trinuclear Zn—Pr—Zn molecule in the asymmetric unit. Besides the coordination environments of the metal atoms, the coordination mode of the carboxylate groups is the same as in the $LaZn_2$ complex. The Pr^{III} and Zn^{II} ions are bridged by three carboxylate groups in the same coordination mode as Pr—O—C—O—Zn. The two Pr···Zn separations are not equal: 4.010 (5) Å for Zn1···Pr and 3.967 (4) Å for Zn2···Pr. The former is shorter than that of Zn1···La in the isomorphous structure and the latter is longer than that of Zn2···La in the isomorphous structure (Zhu *et al.*, 2004).

The six $Pr—O_{carboxylate}$ bond distances are nearly the same [2.394 (3)–2.454 (3) Å] and the average $Pr—O_{nitrate}$ bond length is 2.593 Å. All Pr—O bond distances are shorter than those of La—O in the isomorphous structure, consistent with the characteristic lanthanide contraction. All Zn—O and Zn—N bond distances are nearly the same as those of the isostructural $LaZn_2$ complex, being 2.003 (2)–2.077 (3) Å for Zn—O and 2.093 (3)–2.185 (3) Å for Zn—N.

A comparison of the IR spectrum of $CH_2{=}C(CH_3)COOH$ with those of its complexes reveals that considerable changes in frequencies have occurred due to coordination. A peak assigned as O—H at 1710 cm^{-1} in $CH_2{=}C(CH_3)COOH$ disappears. According to Deacon & Phillips (1980), the separation of the two C—O stretching frequencies ($\Delta\nu$) can be used to distinguish between the different coordination modes of the OCO group (*i.e.* ionic, monodentate or bidentate). In the present case, the $\Delta\nu$ value is 160 cm^{-1}, which is smaller than the value of 170 cm^{-1} for the sodium salt and is indicative of bidentate coordination. However, spectroscopic techniques could not distinguish between carboxylic groups with bridging bidentate and chelating bidentate mode coordination. The IR spectrum also shows peaks due to the ν(C=C) and ν(C—H) vibrations at 1600 and 2970 cm^{-1}, respectively. In any case, the IR spectra are consistent with the structure established by the X-ray diffraction experiment.

Experimental

$PrL_3 \cdot 2H_2O$ [432 mg, 1.0 mmol; H*L* = $CH_2{=}C(CH_3)COOH$] was dissolved in 5 ml of water. 1.0 ml of a 1 *M* solution of $Zn(NO_3)_2$ was added and the pH was adjusted to 4.1 with 0.1 *M* H*L*. An ethanol solution (5 ml) of 2,2′-bipyridine (156 mg, 1.0 mmol) was added to the mixture with stirring. After filtration, the filtrate was allowed to stand at room temperature and single crystals suitable for X-ray work precipitated after a few days. The yield, calculated with respect to the consumed 2,2′-bipyridine, was 47.5%. The elemental analyses on C, H and N were performed using a Carlo–Erba 1110, while elemental analyses for Pr and Zn were made by titration with EDTA. Calculated for $C_{44}H_{46}N_5O_{15}PrZn_2$: C 45.65, H 3.98, N 6.05, Pr 12.18, Zn 11.31%; found: C 45.44, H 4.08, N 5.92, Pr 12.34, Zn 10.93%. IR spectra were recorded with a Nicolet 560 spectrophotometer (4000–400 cm^{-1}), using a powdered sample spread on a KBr plate; IR: ν_{as} (COO) 1574, ν_s (COO) 1414, ν (C=C) 1600 cm^{-1}.

Crystal data

$[PrZn_2(C_4H_5O_2)_6(NO_3)(C_{10}H_8N_2)_2]$
$M_r = 1156.51$
Triclinic, $P\overline{1}$
$a = 11.3602$ (4) Å
$b = 13.7513$ (8) Å
$c = 16.4755$ (10) Å
$\alpha = 104.026$ (1)°
$\beta = 99.319$ (1)°
$\gamma = 100.192$ (3)°
$V = 2400.4$ (2) Å^3

$Z = 2$
$D_x = 1.600$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 9302 reflections
$\theta = 1.3$–27.4°
$\mu = 2.06$ mm^{-1}
$T = 293$ (2) K
Chunk, light green
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.577$, $T_{max} = 0.673$
19000 measured reflections

8562 independent reflections
7539 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.3°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.090$
$S = 1.17$
8562 reflections
604 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 1.031P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Pr—O1	2.594 (3)	Zn1—O11	2.042 (3)
Pr—O2	2.591 (3)	Zn1—O12	2.027 (3)
Pr—O3	2.402 (3)	Zn1—N1	2.172 (3)
Pr—O4	2.394 (3)	Zn1—N2	2.099 (3)
Pr—O5	2.403 (3)	Zn2—O13	2.077 (3)
Pr—O6	2.422 (3)	Zn2—O14	2.003 (2)
Pr—O7	2.454 (3)	Zn2—O15	2.021 (3)
Pr—O9	2.396 (3)	Zn2—N4	2.185 (3)
Zn1—O10	2.009 (3)	Zn2—N5	2.093 (3)

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 the riding model, with $U_{iso}(H) = 1.2$ or 1.5 times U_{eq}(parent atom).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 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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