

Bis(2,2'-bipyridine)-1 κ^2 N:N';3 κ^2 N:N'-hexakis(μ - α -methylacrylato)-1:2 κ^6 O:O';2:3 κ^6 O:O'-nitrate-2 κ^2 O:O'-dizinc(II)neodymium(III)

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å

R factor = 0.039

wR factor = 0.111

Data-to-parameter ratio = 13.9

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

The crystal structure of the title compound, $[\text{NdZn}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$, is made up of discrete molecules of a trinuclear Zn–Nd–Zn complex, with the central Nd atom linked by three bridging bidentate α -methylacrylate groups to each of the two Zn atoms. The title complex is isostructural with its previously reported La and Pr analogues, and the Nd atom has a distorted square-antiprismatic coordination, formed by six O atoms of the bridging methylacrylate groups and two O atoms of a bidentate chelating nitro group. Both of the Zn atoms have a distorted trigonal-bipyramidal coordination, formed by three O atoms of the bridging methylacrylate groups and two N atoms of the chelating 2,2'-bipyridine ligands.

Comment

Although molecular magnetic compounds have been for the most part developed only recently, effective strategies for obtaining new materials with expected properties, such as molecular ferro- and ferrimagnets, organic magnets, single-molecule magnets, high-spin molecules *etc.*, have already been suggested (Miller & Drillon, 2001–2002; Christou *et al.*, 2000). The efforts aimed at preparation of molecular magnets containing rare-earth ions have been comparatively less numerous, because the interactions in pairs of f electrons are expected to be small, producing measurable effects only at extremely low temperatures. However, the number of reported new complexes with rare-earth atoms, magnetically coupled to transition-metal atoms and/or organic radicals, is rapidly increasing (Lescop *et al.*, 1999; Caneschi *et al.*, 2000; Costes *et al.*, 2000; Bencini *et al.*, 2001; Schweizer *et al.*, 2001).

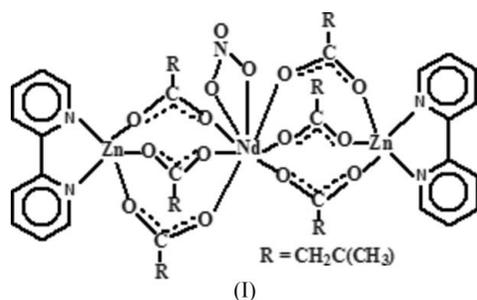
Complexes with different lanthanide metals are in most cases isostructural, if their central atoms have similar coordination environments and have close radii. It is important to elucidate magnetic properties of different $4f$ or $3d$ metallic ions in heteronuclear complexes. We are trying to gain insight into peculiarities of magnetic behaviour of lanthanide-transition metal heteronuclear complexes by synthesizing and studying (using both X-ray diffraction and magnetic measurements) a series of isostructural complexes with varying transition metal atoms, *e.g.* complexes with Ln–Zn, Ln–Cu, Ln–Co and Ln–Ni pairs. The present investigation was undertaken as a part of our ongoing project on the structures and properties of heteronuclear complexes of rare earth and transition metals bridged by carboxylate groups (Wu, Lu, Wu & Zheng, 2003).

Fig. 1 shows the molecular structure of the title complex, (I); selected bond distances and angles are listed in Table 1.

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The title compound is isostructural with its La and Pr analogues, reported by Zhu *et al.* (2004a) and Zhu *et al.* (2004b), respectively. As one would expect, the geometric characteristics of the Nd complex are almost the same as those of the Pr complex and differ more noticeably from the parameters of the La derivative. For a detailed comparison of the structure and IR spectra with those of the La complex, please refer to the *Comment* section of the paper by Zhu *et al.* (2004b). As the geometries of the Pr and Nd complexes are very similar, the discussion of the Pr complex by Zhu *et al.* (2004b) is fully applicable to the title complex as well.

The structure of the title compound is also similar to that of $[\text{NdZn}_2(\text{CH}_2=\text{CMeCOO})_6(\text{NO}_3)(\text{phen})_2]$ (Wu, Lu & Zheng, 2003), which has phenanthroline groups, rather than bipyridine groups, as bidentate chelate ligands on Zn atoms.

Experimental

$\text{NdL}_3 \cdot 2\text{H}_2\text{O}$ [436 mg, 1.0 mmol; HL = $\text{CH}_2\text{C}(\text{CH}_3)\text{COOH}$] was dissolved in water (5 ml). A 1M solution of $\text{Zn}(\text{NO}_3)_2$ (1.0 ml) was added and the pH was adjusted to 4.1 with 0.1 M HL. An ethanol solution (5 ml) of 2,2'-bipyridine (156 mg, 1.0 mmol) was added to the mixture with stirring. The filtrate was allowed to stand at room temperature, and single crystals suitable for X-ray analysis precipitated after a few days. The yield, as calculated with respect to the consumed 2,2'-bipyridine, is 44%. Analysis calculated for $\text{C}_{44}\text{H}_{46}\text{N}_5\text{NdO}_{15}\text{Zn}_2$: C 45.56, H 3.97, N 6.04, Nd 12.44, Zn 11.28%; found: C 45.55, H 4.01, N 6.14, Nd 12.26, Zn 11.35%. IR: $\nu_{\text{as}}(\text{COO})$ 1574, $\nu_{\text{s}}(\text{COO})$ 1408, $\nu(\text{C}=\text{C})$ 1659, $\nu(\text{C}-\text{H})$ 2970 cm^{-1} .

Crystal data

$[\text{NdZn}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$	$Z = 2$
$M_r = 1159.84$	$D_x = 1.605 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.3751(9) \text{ \AA}$	Cell parameters from 8348 reflections
$b = 13.7258(8) \text{ \AA}$	$\theta = 2.5\text{--}27.5^\circ$
$c = 16.4798(11) \text{ \AA}$	$\mu = 2.13 \text{ mm}^{-1}$
$\alpha = 103.903(4)^\circ$	$T = 293(2) \text{ K}$
$\beta = 99.490(4)^\circ$	Chunk, pink
$\gamma = 100.168(5)^\circ$	$0.30 \times 0.30 \times 0.20 \text{ mm}$
$V = 2399.9(3) \text{ \AA}^3$	

Data collection

Rigaku R-Axis RAPID diffractometer	8421 independent reflections
ω scans	7077 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.568$, $T_{\text{max}} = 0.675$	$\theta_{\text{max}} = 25.1^\circ$
18091 measured reflections	$h = -13 \rightarrow 13$
	$k = -16 \rightarrow 16$
	$l = -19 \rightarrow 19$

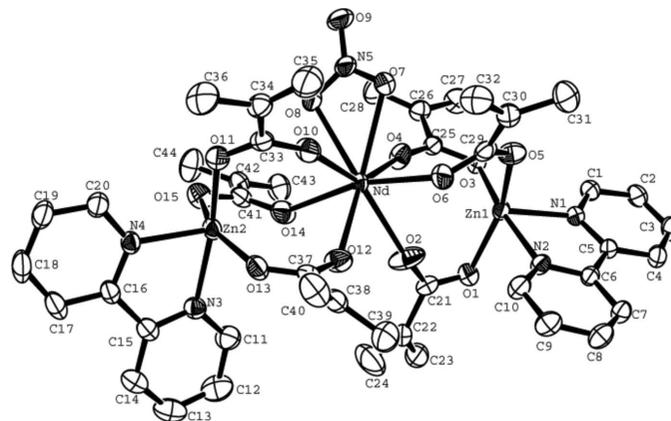


Figure 1

The molecule of the title complex, with displacement ellipsoids drawn at the 30% probability level. The H atoms have been omitted.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.111$
 $S = 1.01$
 8421 reflections
 605 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 3.3948P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0053 (4)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Nd—O2	2.438 (4)	Zn1—O3	2.005 (3)
Nd—O4	2.393 (4)	Zn1—O5	2.024 (4)
Nd—O6	2.380 (4)	Zn1—N1	2.097 (4)
Nd—O7	2.570 (4)	Zn1—N2	2.192 (4)
Nd—O8	2.579 (4)	Zn2—O11	2.008 (4)
Nd—O10	2.393 (4)	Zn2—O13	2.029 (4)
Nd—O12	2.407 (4)	Zn2—O15	2.045 (4)
Nd—O14	2.382 (4)	Zn2—N3	2.171 (5)
Zn1—O1	2.073 (4)	Zn2—N4	2.104 (4)
O2—Nd—O4	72.96 (15)	O8—Nd—O14	74.04 (14)
O2—Nd—O6	79.27 (19)	O10—Nd—O12	72.84 (14)
O2—Nd—O7	133.17 (17)	O10—Nd—O14	90.28 (16)
O2—Nd—O8	141.40 (16)	O12—Nd—O14	79.08 (15)
O2—Nd—O10	143.61 (15)	O1—Zn1—O3	95.52 (15)
O2—Nd—O12	71.50 (16)	O1—Zn1—O5	155.69 (17)
O2—Nd—O14	89.97 (19)	O1—Zn1—N1	100.83 (15)
O4—Nd—O6	92.39 (15)	O1—Zn1—N2	86.54 (16)
O4—Nd—O7	72.58 (15)	O3—Zn1—O5	95.04 (15)
O4—Nd—O8	73.61 (13)	O3—Zn1—N1	95.45 (14)
O4—Nd—O10	143.20 (14)	O3—Zn1—N2	171.61 (14)
O4—Nd—O12	143.86 (14)	O5—Zn1—N1	99.89 (17)
O4—Nd—O14	94.60 (15)	O5—Zn1—N2	86.19 (16)
O6—Nd—O7	71.52 (14)	N1—Zn1—N2	76.16 (15)
O6—Nd—O8	120.90 (14)	O11—Zn2—O13	89.89 (17)
O6—Nd—O10	92.15 (17)	O11—Zn2—O15	96.83 (18)
O6—Nd—O12	87.37 (16)	O11—Zn2—N3	167.84 (17)
O6—Nd—O14	164.87 (14)	O11—Zn2—N4	93.33 (17)
O7—Nd—O8	49.40 (14)	O13—Zn2—O15	155.01 (17)
O7—Nd—O10	74.37 (13)	O13—Zn2—N3	86.48 (16)
O7—Nd—O12	139.97 (15)	O13—Zn2—N4	104.27 (15)
O7—Nd—O14	123.43 (14)	O15—Zn2—N3	91.29 (17)
O8—Nd—O10	72.79 (14)	O15—Zn2—N4	99.36 (16)
O8—Nd—O12	135.72 (13)	N3—Zn2—N4	76.38 (17)

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 model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ of the corresponding carrier atom [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ in the case of the methyl H atoms].

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Bencini, A., Daul, C. A., Dei, A., Mariotti, F., Hyoyoung, L., Shultz, D. A. & Sorace, L. (2001). *Inorg. Chem.* **40**, 1582–1590.
- Caneschi, A., Dei, A., Gatteschi, D., Sorace, L. & Vostrikova, K. (2000). *Angew. Chem. Int. Ed. Engl.* **39**, 246–248.
- Christou, G., Gatteschi, D., Hendrickson, D. N. & Sessoli, R. (2000). *MRS Bull.* **25**, 66–71.
- Costes, J.-P., Dahan, F., Dupuis, A. & Laurent, J.-P. (2000). *Inorg. Chem.* **39**, 169–173.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Lescop, C., Luneau, D., Belorisky, E., Fries, P., Guillot, M. & Rey, P. (1999). *Inorg. Chem.* **38**, 5472–5473.
- Miller, J. S. & Drillon, M. (2001–2002). *Magnetism: Molecules to Materials I–III*. Weinheim: Wiley-VCH.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSK (2002). *CrystalStructure*. Version 3.00. Rigaku/MSK, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Schweizer, J., Bencini, A., Carbonera, C., Epstein, A. J., Golhen, S., Lelièvre-Berna, E., Miller, J. S., Ouahab, L., Pontillon, Y., Ressouche, E. & Zheludev, A. (2001). *Polyhedron*, **20**, 1771–1778.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Wu, B., Lu, W. M., Wu, F. F. & Zheng, X. M. (2003). *Transition Met. Chem.* **28**, 694–697.
- Wu, B., Lu, W. M. & Zheng, X. M. (2003). *J. Chem. Crystallogr.* **33**, 203–207.
- Zhu, Y., Lu, W. M. & Chen, F. (2004a). *Acta Cryst.* **E60**, m963–m965.
- Zhu, Y., Lu, W. M. & Chen, F. (2004b). *Acta Cryst.* **E60**, m1459–m1461.