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Bis(μ-2,6-diformyl-4-methylphenolato)-bis[bis(2,6-diformyl-4-methylphenolato)-neodymium(III)]

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The title compound, $[Nd_2(C_9H_7O_3)_6]$, crystallizes from an anhydrous alcoholic mixture of neodymium perchlorate, 2,6-diformyl-4-methylphenol and sodium hydroxide. The structure consists of discrete dinuclear molecules with Nd^{III} ions in eightfold coordination environments. The complete molecule is generated from the asymmetric unit by a crystallographic center of symmetry. Intramolecular and intermolecular π–π stacking and C—H···O interactions help to stabilize the crystal packing.

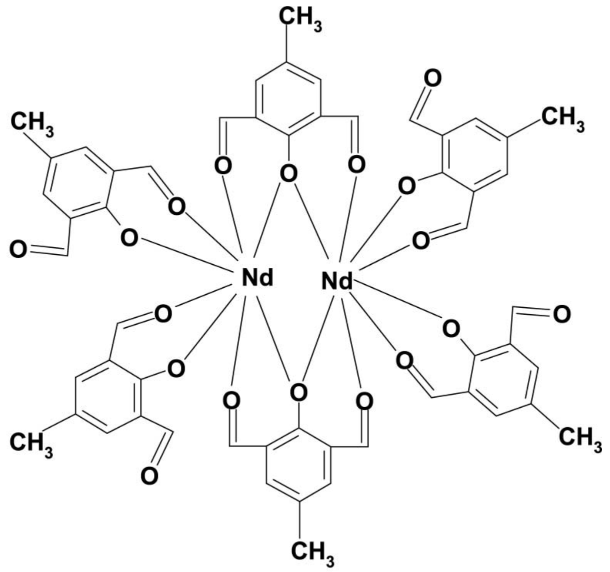
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.094
Data-to-parameter ratio = 12.4

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

Comment

Lanthanide(III) dinuclear compounds which feature well isolated Ln^{3+}–Ln^{3+} pairs are suitable building blocks for the assembly of Ln^{III} nanoclusters (Zheng, 2001) and ideal models for the study of metal–metal interactions in these polynuclear complexes (Thompson *et al.*, 2001). The title compound, (I), was synthesized during attempts to build dinuclear complexes (Kahwa *et al.*, 1989) that could facilitate a comparative study of the synthesis and electronic properties of Ln^{III} nanoclusters.



(I)

In (I), each Nd^{III} ion is coordinated by ligating carbonyl and phenolate O atoms from two bridging and two bidentate 2,6-diformyl-4-methylphenol ligands to give each metal ion an eightfold coordination environment of approximate D_{4d} symmetry (Fig. 1). The complete molecule is generated by a crystallographic inversion center which is located at the center of the four-membered Nd_2O_2 ring (Fig. 1). The bond distances and angles (Table 1) are similar to those obtained for other

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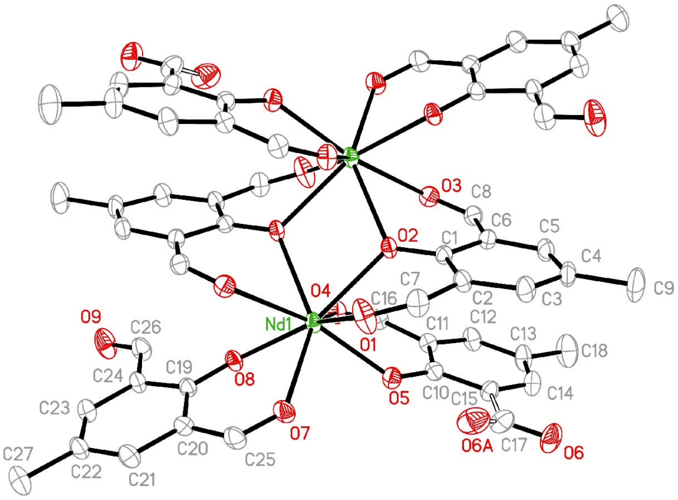

Figure 1
View of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are not shown. Unlabeled atoms are related to labeled atoms by the symmetry operator ($-x$, $1-y$, $-z$). Both disorder components are shown.

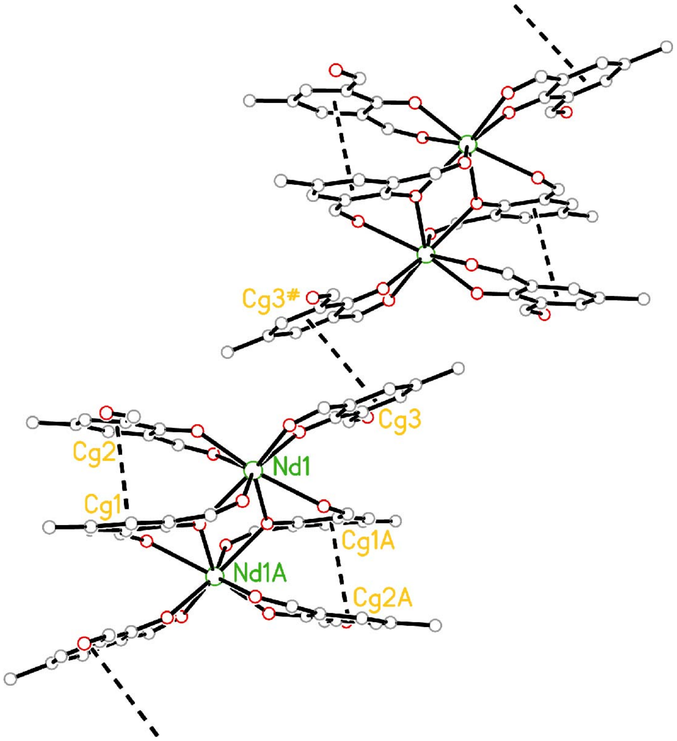

Figure 2
Part of the crystal structure of (I), showing the π–π stacking interactions as dashed lines. *Cg*1, *Cg*2 and *Cg*3 are defined as the centroids of rings C1–C6, C10–C15 and C19–C24, respectively. Atoms labelled with 'A' and '#' are related by the symmetry codes ($-x$, $1-y$, $-z$) and ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$), respectively.

lanthanide(III) complexes containing a bridging Ln_2O_2 ring (Howell *et al.*, 1996). The $Nd1\cdots Nd1^i$ separation (see Table 1 for symmetry code) in (I) is 4.0424 (5) Å.

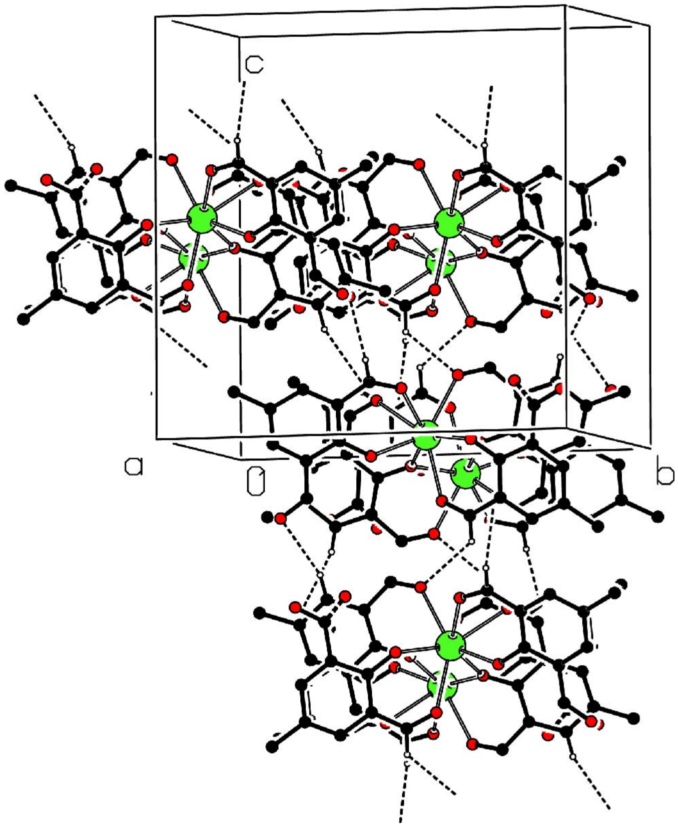

Figure 3
A view of (I), showing weak C—H$\cdots$O interactions as dashed lines. Colour codes: green Nd, red O and black C. H atoms not involved in hydrogen bonding have been omitted.

In the crystal structure of (I), there are significant intra- and intermolecular π–π interactions. The intramolecular $Cg1\cdots Cg2$ distance is 3.698 Å, with a perpendicular distance of 3.314 Å, where *Cg*1 and *Cg*2 are the centroids of rings C1–C6 and C10–C15, respectively. In addition, intermolecular π–π interactions [$Cg3\cdots Cg3^{v}$ = 3.653 (4) Å and perpendicular distance = 3.440 Å, where *Cg*3 is the centroid of ring C19–C24; symmetry code: (v) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$] link molecules into extended chains along [$\overline{1}10$] (see Fig. 2). A three-dimensional network is formed when these chains are connected by weak C—H$\cdots$O intermolecular interactions (Table 2 and Fig. 3).

This study indicates that compounds of this type are ideal for studying the electronic interactions in well isolated Ln^{III}–Ln^{III} pairs.

Experimental

$Nd(ClO_4)_3\cdot nH_2O$ (0.12 mmol in 20 ml anhydrous ethanol) was added to a mixture of 2,6-diformyl-4-methylphenol (0.35 mmol) and NaOH (0.35 mmol) in anhydrous methanol (25 ml). The clear yellow solution was left to evaporate slowly on a hotplate at 333 K. After 1 d, yellow needles of (I) were recovered in 42% yield.

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Crystal data

$[Nd_2(C_9H_7O_3)_6]$
$M_r = 1267.36$
Monoclinic, $C2/c$
$a = 21.1211$ (6) Å
$b = 15.0486$ (4) Å
$c = 15.5611$ (5) Å
$\beta = 97.181$ (1)°
$V = 4907.2$ (2) Å^3
$Z = 4$

$D_x = 1.715$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4265 reflections
$\theta = 2.6$–25.0°
$\mu = 2.17$ mm^{-1}
$T = 150$ (1) K
Cut needle, yellow
$0.08 \times 0.05 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.846$, $T_{max} = 0.918$
14613 measured reflections

4319 independent reflections
3340 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 25.0°$
$h = -25 \rightarrow 25$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.07$
4319 reflections
348 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 5.4862P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00056 (10)

Table 1
Selected geometric parameters (Å, °).

Nd1—O5	2.293 (4)	Nd1—O7	2.466 (3)
Nd1—O8	2.293 (3)	Nd1—O4	2.489 (4)
Nd1—O2^i	2.428 (3)	Nd1—O1	2.511 (4)
Nd1—O2	2.463 (3)	Nd1—O3^i	2.593 (4)
O5—Nd1—O8	110.43 (13)	O7—Nd1—O4	131.38 (13)
O5—Nd1—O2^i	137.49 (11)	O5—Nd1—O1	81.59 (14)
O8—Nd1—O2^i	86.93 (12)	O8—Nd1—O1	138.96 (12)
O5—Nd1—O2	80.53 (12)	O2^i—Nd1—O1	110.92 (14)
O8—Nd1—O2	150.67 (11)	O2—Nd1—O1	67.95 (12)
O2^i—Nd1—O2	68.52 (13)	O7—Nd1—O1	71.14 (14)
O5—Nd1—O7	82.02 (13)	O4—Nd1—O1	139.26 (12)
O8—Nd1—O7	72.01 (13)	O5—Nd1—O3^i	153.59 (11)
O2^i—Nd1—O7	140.35 (12)	O8—Nd1—O3^i	74.94 (12)
O2—Nd1—O7	137.31 (12)	O2^i—Nd1—O3^i	67.03 (11)
O5—Nd1—O4	71.25 (12)	O2—Nd1—O3^i	107.71 (11)
O8—Nd1—O4	80.22 (12)	O7—Nd1—O3^i	75.08 (12)
O2^i—Nd1—O4	74.23 (12)	O4—Nd1—O3^i	134.51 (12)
O2—Nd1—O4	77.88 (11)	O1—Nd1—O3^i	78.71 (13)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O9^{ii}	0.95	2.59	3.497 (7)	160
C16—H16A···O1^{iii}	0.95	2.50	3.176 (6)	128
C25—H25A···O6^{iv}	0.95	2.43	3.349 (8)	162

Symmetry codes: (ii) $x, 1-y, \frac{1}{2}+z$; (iii) $x, 1-y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

All H atoms were placed in calculated positions, with C—H distances of 0.95 (phenyl) and 0.98 Å (methyl), and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier).

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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