Tetrakis(μ_2-2,6-diformyl-4-methylphenolato)tetra-μ_3-hydroxo-tetrakis[diaquaneodymium(III)] tetrakis(perchlorate) ethanol disolvate

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The title compound, $[Nd_4(\mu_2\text{-}C_9H_7O_3)_4(\mu_3\text{-OH})_4(H_2O)_8]$-$(ClO_4)_4\cdot 2C_2H_6O$, was synthesized from the ligand-controlled hydrolysis of $Nd(ClO_4)_3$. The cation, which lies on a crystallographic twofold axis, has four ninefold coordinated Nd^{III} ions and four triply bridging hydroxy groups occupying alternate vertices of a distorted cube and supported by four $\mu_2\text{-}C_9H_7O_3$ ligands. The crystal structure indicates that 2,6-diformyl-4-methylphenol is a useful supporting ligand in the synthesis of high-nuclearity Ln^{III} clusters.

Comment

There is currently tremendous interest in the synthesis and characterization of finite polylanthanide(III) entities with nanoscopic dimensions (Zheng, 2001; Wang *et al.*, 2002). This interest lies in several application fields, since lanthanide clusters are potential precursors for ceramics, catalysts and thin-film coatings (Hubert-Pfalzgraf, 1995). Nanoclusters with mutually interacting Ln^{III} ions are also expected to yield new materials with greater versatility resulting from unusual enhancements in magnetic, catalytic, optical and electronic properties (Thompson *et al.*, 2003, 2001). The title compound, (I), is one of a series of similar Ln^{III} compounds synthesized in an investigation into the formation chemistry of nanoclusters which feature commonly encountered aggregation motifs such as $[Ln_4(OH)_4]^{8+}$. We have previously determined the structure of the cation in the title structure as the trifluoromethanesulfonate (Singh-Wilmot *et al.*, 2005).

(I)
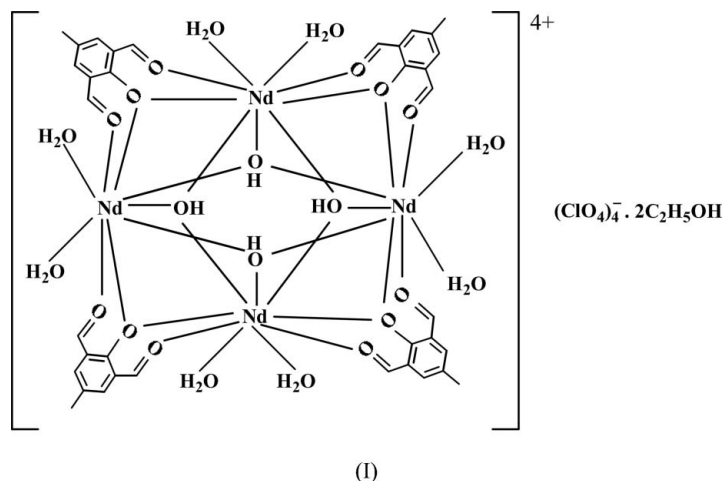
The cation in (I) features four Nd^{III} and four μ_3-hydroxo groups occupying alternate vertices of a distorted cube (Fig. 1). Selected bond distances are given in Table 1. Each Nd^{III} ion is in a ninefold coordination polyhedron of an approximate

tricapped trigonal prism and approximate D_{3h} symmetry, with a shortest metal–metal contact of Nd2$\cdots$Nd2^i = 3.7003 (4) Å [symmetry code: (i) $-x, y, \frac{1}{2} - z$]. This distance is comparable with metal–metal distances seen in other complexes containing a similar cubane-type [Ln$_4(\mu_3$-OH)$_4$]$^{8+}$ core, for example ca 3.83 Å for the shortest Sm$\cdots$Sm distance in [Sm$_4(\mu_3$-OH)$_4$(Gly)$_5$(H$_2$O)$_{11}$]) (Evans $et\ al.$, 2000). Nd—O(phenolate) distances are in the range 2.546 (3)–2.597 (3) Å, while the Nd—O(carbonyl) distances are in the range 2.441 (4)–2.484 (4) Å. The range of Nd—O(μ_3-OH) distances [2.393 (3)–2.472 (3) Å] compares well with those in [Nd$_4(\mu_3$-OH)$_4$(Ala)$_6$(H$_2$O)$_{10}$] (ca 2.43 Å; Zheng & Wang, 2000).

Experimental

NaOH (2 mmol, 0.08 g) in methanol (10 ml) was added in five portions to a boiling solution of Nd(ClO$_4$)$_3$.nH$_2$O (8 mmol, 1.346 g Nd$_2$O$_3$) in methanol (10 ml). A solution of 2,6-diformyl-4-methylphenol (4 mmol, 0.6566 g) and NaOH (4 mmol, 0.16 g) in methanol (150 ml) was then added to the boiling solution in 20 ml portions. After each addition of sodium cresolate, the mixture was boiled until approximately 10 ml of solution remained before adding the next 20 ml portion. The pH of the mixture at this point was approximately 6.5. The final mixture was boiled until 5 ml of solution remained. It was then cooled and filtered and approximately 10 ml of ethanol was added. The resulting mixture was left in an open flask at room temperature. The onset of crystallization was obvious after 3 d but a further 2 d were allowed for the process to proceed to completion. Yellow blocks of (I) were recovered in 20% yield (calculation based on Ln^{III}). The crystals lost solvent and crumbled to an amorphous solid on exposure to air. CAUTION: Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Crystal data

[Nd$_4$(C$_9$H$_7$O$_3$)$_4$(OH)$_4$(H$_2$O)$_8$]-(ClO$_4$)$_4$·2C$_2$H$_6$O	D_x = 1.620 Mg m^{-3}
M_r = 1931.64	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 8715
a = 20.9933 (3) Å	reflections
b = 24.7385 (5) Å	θ = 2.6–27.5°
c = 17.6893 (3) Å	μ = 2.80 mm^{-1}
β = 120.469 (1)°	T = 150 (1) K
V = 7918.1 (2) Å^3	Block, yellow
Z = 4	0.32 × 0.28 × 0.25 mm

Data collection

Bruker Nonius KappaCCD area detector diffractometer	8998 independent reflections
	7708 reflections with $I > 2\sigma(I)$
φ scans and ω scans with κ offsets	R_{int} = 0.037
Absorption correction: multi-scan	θ_{max} = 27.5°
(*DENZO-SMN*; Otwinowski &	$h = -27 \rightarrow 27$
Minor, 1997)	$k = -32 \rightarrow 32$
T_{min} = 0.430, T_{max} = 0.497	$l = -22 \rightarrow 19$
31251 measured reflections	

Refinement

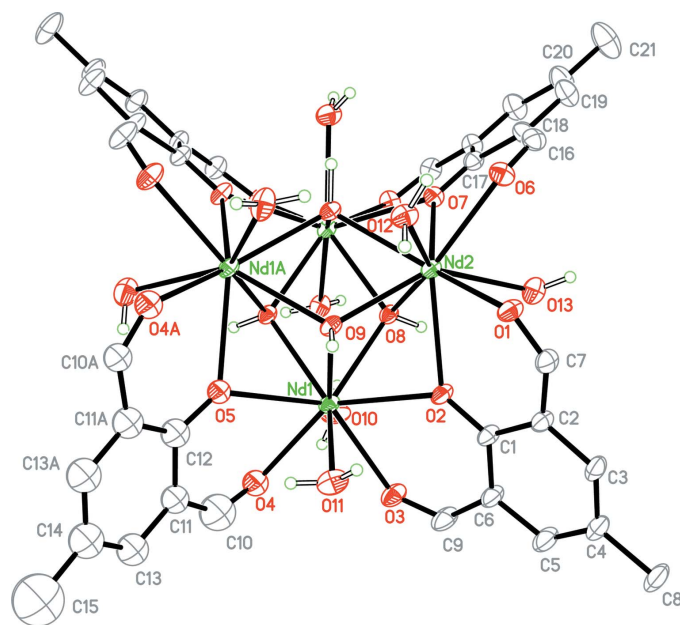|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.043	$+ 41.2001P]$
$wR(F^2)$ = 0.122	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max} < 0.001$
8998 reflections	$\Delta\rho_{max}$ = 1.64 e Å^{-3}
400 parameters	$\Delta\rho_{min}$ = −1.16 e Å^{-3}
H-atom parameters constrained	

Figure 1
A view of the cation of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms are not shown. Atoms labelled with the suffix A are related by the symmetry operator ($-x, y, -z + \frac{1}{2}$). Only one disorder component is shown.

Table 1
Selected bond lengths (Å).

Nd1—O9	2.416 (3)	Nd2—O8	2.392 (3)
Nd1—O4A^i	2.429 (12)	Nd2—O6	2.441 (4)
Nd1—O4	2.456 (12)	Nd2—O9	2.447 (3)
Nd1—O9^i	2.467 (3)	Nd2—O1	2.452 (3)
Nd1—O8	2.472 (3)	Nd2—O8^i	2.453 (3)
Nd1—O10	2.478 (4)	Nd2—O13	2.516 (4)
Nd1—O3	2.484 (4)	Nd2—O7	2.559 (3)
Nd1—O11	2.512 (3)	Nd2—O2	2.597 (3)
Nd1—O2	2.546 (3)	Nd2—O12	2.627 (3)
Nd1—O5	2.565 (3)		

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.

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

$D-$H$\cdots A$	$D-$H	H$\cdots A$	$D\cdots A$	$D-$H$\cdots A$
O8—H8$\cdots$O19^i	1.00	1.98	2.969 (10)	168
O9—H9$\cdots$O15^i	1.00	1.93	2.922 (7)	170
O10—H10$C\cdots$O3^{ii}	0.84	2.05	2.884 (5)	170
O10—H10$D\cdots$O12^i	0.84	1.98	2.764 (5)	155
O11—H11$A\cdots$O14^i	0.84	2.49	3.331 (14)	180
O12—H12$A\cdots$O19A	0.84	2.10	2.945 (8)	180
O12—H12$B\cdots$O16^i	0.84	1.98	2.819 (6)	180
O13—H13$C\cdots$O20^i	0.84	2.01	2.845 (12)	180
O13—H13$D\cdots$O19A^{iii}	0.84	2.10	2.943 (8)	180

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

One of the perchlorate anions (Cl2/O18/O19/O20/O21) is disordered over two sites, with an occupancy ratio of 0.577 (4)/0.423 (4) for the major and minor components. Both components of the disorder have the site of O18 in common. In addition, one of the μ_2-C$_9$H$_7$O$_3$ ligands (containing the benzene ring C11/C11A/C12/C13/C13A/C14)

is also disordered; initial refinement gave equal values within experimental error for the two disorder components; the occupancy ratio was therefore fixed at 0.5:0.5 in the final cycles. This disordered ligand is bisected by the crystallographic twofold axis but the disorder is not imposed by the crystallographic symmetry. All H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.95 or 0.98 Å (methyl), and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl H atoms. The H atoms of the bridging hydroxyl ligands were included with O—H = 1.00 Å and $U_{iso}(H) = 1.2U_{eq}(O)$. All other H atoms bonded to O atoms were placed in calculated positions based on an ideal location for O—H···O hydrogen bonding. The O—H distance was fixed at 0.84 Å with $U_{iso}(H) = 1.5U_{eq}(O)$. During the refinement, areas of electron density were located in difference Fourier maps that were assigned as ethanol solvent molecules. The peak pattern of electron density suggested that the solvent molecules were highly disordered, and attempts to model the disorder were unsuccessful. In the final cycles of refinement, the contribution to electron density corresesponding to the disordered ethanol molecules was removed from the observed data using the SQUEEZE option in *PLATON* (Spek, 2003). The resulting data vastly improved the precision of the geometric parameters of the remaining structure. The contributions of two molecules of ethanol have been included in the molecular formula. The hydroxy groups of the ethanol molecules, if present, would contribute to the hydrogen-bonding motif, and for this reason the hydrogen bonding in the title structure is not discussed in detail. In the final difference Fourier map, the three largest density peaks in the range 1.64–1.06 e Å^3 are located within 1.23 Å of the disordered perchlorate anion, and the deepest hole of −1.16 e Å^3 is 0.80 Å from Nd1.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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