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Octaaquatetrakis(μ_2-2,6-diformyl-4-methylphenolato)-tetra-μ_3-hydroxo-tetraneodymium(III) trifluoromethanesulfonate butanol disolvate tetrahydrate

Marvadeen A. Singh-Wilmot,[a]* Ishenkumba A. Kahwa[a] and Alan J. Lough[b]

[a]Chemistry Department, University of the West Indies, Mona Campus, Kingston 7, Jamaica, and [b]Department of Chemistry, University of Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail:
marvadeen.singhwilmot@uwimona.edu.jm

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Key indicators

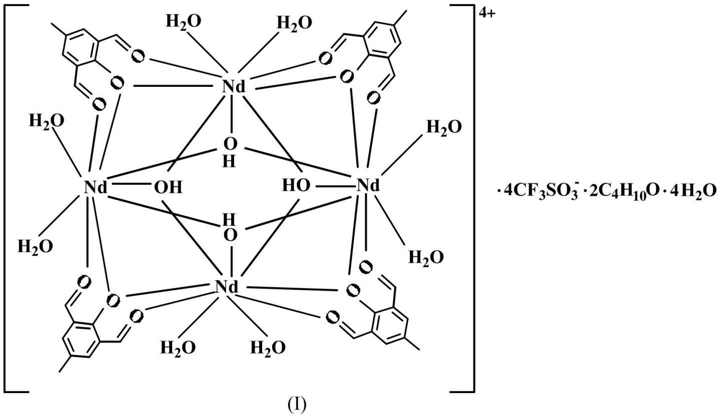
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.010 Å
Some non-H atoms missing
Disorder in solvent or counterion
R factor = 0.049
wR factor = 0.122
Data-to-parameter ratio = 19.9

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

The title compound, $[Nd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}C_9H_7O_3)_4(H_2O)_8](CF_3SO_3)_4\cdot 2C_4H_{10}O\cdot 4H_2O$, was synthesized from $Nd(CF_3SO_3)_3$ and 2,6-diformyl-4-methylphenol at relatively high pH. The cation, which lies on a crystallographic twofold axis, features a cubane-type $[Ln_4(OH)_4]^{8+}$ core of four Nd^{III} cations and four μ_3-OH ligands occupying alternate vertices of a distorted cube.

Comment

We have investigated the effect of counter-anions on the formation of Ln^{III} nanoclusters, including the commonly encountered cubane-type $[Ln_4(OH)_4]^{8+}$ cluster, by hydrolyzing $NdCl_3$, $Nd(NO_3)_3$, $Nd(ClO_4)_3$ and $Nd(CF_3SO_3)_3$ in the presence of 2,6-diformyl-4-methylphenol. In the case of the chlorides and nitrates, yellow polycrystalline compounds formed, but these proved difficult to purify by recrystallization. However, by using $Nd(CF_3SO_3)_3$, the complex cation $[Nd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}C_9H_7O_3)_4(H_2O)_8]^{4+}$ (Fig. 1) was obtained as a component of $[Nd_4(\mu_3\text{-}OH)_4(\mu_2\text{-}C_9H_7O_3)_4(H_2O)_8](CF_3SO_3)_4\cdot 2C_4H_{10}O\cdot 4H_2O$, (I). A similar compound also crystallizes when using $Nd(ClO_4)_3$ (Singh-Wilmot, 2002). In (I), each Nd^{III} ion is bis-chelated by two μ_2-2,6-diformyl-4-methylphenolato ligands, monocoordinated by three μ_3-OH ligands and achieves a coordination number of nine by coordination of two water molecules. The symmetry of the coordination polyhedron is tricapped trigonal prismatic with approximate D_{3h} local symmetry. Bond distances and bond angles in (I) (Table 1) are comparable to those observed in similar compounds (Singh-Wilmot, 2002; Evans *et al.*, 2000; Zheng & Wang, 2000).



(I)

In the crystal structure, both H atoms of each of the coordinated water molecules and the H atoms of the bridging hydroxy group are involved in O—H···O hydrogen bonding.

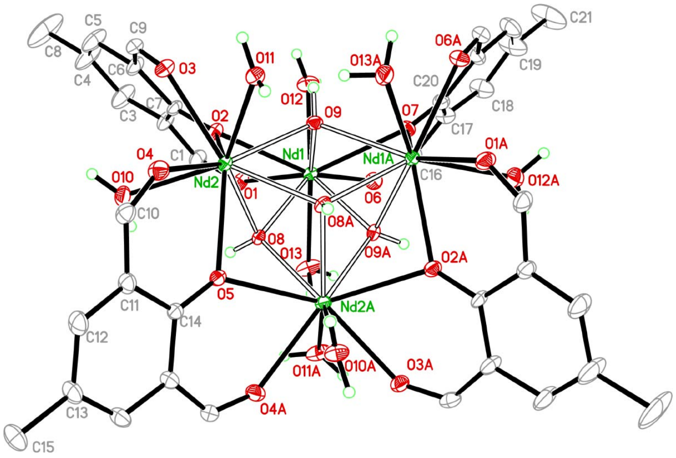


Figure 1
View of the cation of (I), with ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms are not shown. Atoms labeled with the suffix A are related by the symmetry operator $(1 - x, y, -z + \frac{1}{2})$.

For each of the uncoordinated solvent water molecules, one of the H atoms contributes to O—H···O hydrogen bonding but the other is involved in an O—H···π interaction involving the delocalized electrons of the benzene ring and the formyl groups; the closest contact is defined as the distance of the H atom to the phenolic C atom (Table 2).

Experimental

NaOH (2 mmol, 0.08 g) in methanol (10 ml) was added in five portions to a boiling solution of $Nd(CF_3SO_3)_3$ (8 mmol, 1.346 g of Nd_2O_3) in methanol (10 ml). 2,6-Diformyl-4-methylphenol (4 mmol, 0.6566 g) and NaOH (4 mmol, 0.16 g) in methanol (150 ml) were then added to the boiling solution in 20 ml portions. After each 20 ml portion, the mixture was boiled until approximately 10 ml of solution remained before subsequent 20 ml portions were added. The pH of the mixture at this point was approximately 6.5. The final mixture was boiled until 5 ml of solution remained, cooled and filtered, and butan-2-ol (approximately 10 ml) was added. The reaction mixture was left in an open flask at room temperature; yellow cuboidal crystals of (I) were recovered in *ca* 25% yield after 5 d.

Crystal data

$[Nd_4(OH)_4(C_9H_7O_3)_4(H_2O)_8]$-$(CF_3SO_3)_4\cdot 2C_4H_{10}O\cdot 4H_2O$
$M_r = 2258.29$
Monoclinic, $C2/c$
$a = 24.0937$ (4) Å
$b = 24.6345$ (5) Å
$c = 16.7428$ (3) Å
$\beta = 117.3750$ (11)°
$V = 8824.6$ (3) Å^3
$Z = 4$

$D_x = 1.700$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 049 reflections
$\theta = 2.6$–27.5°
$\mu = 2.52$ mm^{-1}
$T = 150$ (1) K
Cuboid, yellow
0.32 × 0.28 × 0.26 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
$T_{min} = 0.456$, $T_{max} = 0.517$
38 049 measured reflections
10 085 independent reflections

9158 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.5°$
$h = -31 \rightarrow 27$
$k = -31 \rightarrow 31$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.122$
$S = 1.23$
10 085 reflections
508 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 141.614P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.38$ e Å^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Nd1—O9	2.414 (4)	Nd2—O9	2.425 (4)
Nd1—O9^{i}	2.436 (4)	Nd2—O8	2.428 (4)
Nd1—O8	2.448 (4)	Nd2—O8^{i}	2.435 (4)
Nd1—O6	2.467 (4)	Nd2—O4	2.464 (4)
Nd1—O12	2.493 (4)	Nd2—O3	2.470 (4)
Nd1—O1	2.494 (4)	Nd2—O10	2.480 (4)
Nd1—O2	2.536 (4)	Nd2—O11	2.554 (5)
Nd1—O7	2.549 (4)	Nd2—O5	2.591 (4)
Nd1—O13	2.562 (5)	Nd2—O2	2.596 (4)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8O···O18	0.83 (5)	2.10 (6)	2.891 (13)	158 (7)
O9—H9O···O15	0.83 (5)	2.19 (6)	2.982 (6)	159 (6)
O10—H10*D*···O18	0.84	1.89	2.729 (11)	180
O10—H10*E*···O1*W*^{ii}	0.84	1.98	2.816 (6)	180
O11—H11*D*···O1*W*	0.84	2.10	2.937 (7)	179
O11—H11*E*···O19^{i}	0.84	2.12	2.955 (11)	180
O12—H12*D*···O16	0.84	1.95	2.794 (7)	180
O12—H12*E*···O2*W*^{iii}	0.84	1.97	2.806 (7)	180
O13—H13*D*···O11^{i}	0.84	1.86	2.698 (7)	180
O13—H13*E*···O2*W*^{i}	0.84	2.02	2.862 (8)	180
O1*W*—H1*WA*···O14	0.84	2.01	2.850 (8)	180
O1*W*—H1*WB*···C9^{ii}	0.84	2.33	3.167 (8)	180
O2*W*—H2*WA*···O15	0.84	2.19	3.034 (8)	180
O2*W*—H2*WB*···C16^{iv}	0.84	2.44	3.276 (8)	180

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

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 $U_{iso}(H) = 1.2U_{eq}(C)$ [$U_{iso}(H) = 1.5U_{eq}(C)$ for methyl]. The H atoms of the bridging hydroxy ligands were located in a difference Fourier map and refined independently with $U_{iso}(H) = 1.2U_{eq}(O)$. 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 $U_{iso}(H) = 1.2U_{eq}(O)$. During the refinement, areas of electron density were located in difference Fourier maps that were assigned as butanol 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 corresponding to the disordered butanol 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 butanol have been included in the

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molecular formula. The hydroxy groups of the butanol molecules, if present, would contribute to the hydrogen-bonding motif, and for that reason the hydrogen bonding in the title structure is not discussed in detail even though every hydrogen-bond donor–acceptor interaction is satisfied. In the final difference map, the largest density peak was located 0.89 Å from S2 and the deepest hole was 0.96 Å from Nd2.

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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References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Evans, W. J., Greci, M. A. & Ziller, J. W. (2000). *Inorg. Chem.* **39**, 3213–3220.

Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.12, Windows NT Version. Bruker AXS Inc., Madison, USA.

Singh-Wilmot, M. A. (2002). PhD thesis, University of the West Indies, Jamaica.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Zheng, Z. & Wang, R. (2000). *Comments Inorg. Chem.* **22**, 1–30.

m972 Singh-Wilmot *et al.* • $[Nd_4(OH)_4(C_9H_7O_3)_4(H_2O)_8](CF_3SO_3)_4$ *Acta Cryst.* (2005). E**61**, m970–m972