

Poly[[aquaneodymium(III)]- μ_3 -decane-1,10-dicarboxylato- μ_3 -9-carboxynonanecarboxylato]

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The title compound, $[\text{Nd}(\text{C}_{10}\text{H}_{16}\text{O}_4)(\text{C}_{10}\text{H}_{17}\text{O}_4)(\text{H}_2\text{O})]_n$, has a novel Nd–organic framework constructed from sebacic acid ($\text{C}_{10}\text{H}_{18}\text{O}_4$) linkers, the longest aliphatic ligand used to date in lanthanide metal–organic framework compounds. The structure contains edge-shared chains of $\text{NdO}_8(\text{H}_2\text{O})$ tricapped trigonal prisms that propagate in the [100] direction, with Nd–O distances in the range 2.414 (4)–2.643 (4) Å.

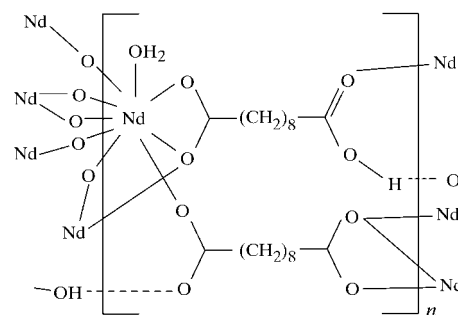
Comment

Metal–organic frameworks (MOFs) have been the subject of increased study recently, due to their potential for designed architectures and their unique applicability to separations, gas storage, molecular recognition and catalysis (Moulton & Zaworotko, 2001). A subset of these materials are lanthanide-containing MOFs, the structures of which have the potential for unique topologies when one considers the rich and variable coordination chemistry of the Ln elements. Furthermore, the luminescent properties of these compounds, which result from Ln f – f electronic transitions, are being exploited for possible sensing applications (Ma *et al.*, 1999).

A representative survey of Ln-MOFs with aliphatic carboxylate linkers reported since 1998 reveals some recurring structural features with respect to the building units of these materials (Dimos *et al.*, 2002; Głowiak *et al.*, 1986; Kim *et al.*, 2004; Kiritsis *et al.*, 1998; Michaelides *et al.*, 2003; Serpaggi & Ferey, 1998; Vaidhyanathan *et al.*, 2002). For example, many Ln-MOFs contain zero-dimensional Ln building units or isolated metal centers. That is, a single Ln ion (or at most a dimer) is coordinated to multifunctional organic linkers and/or water molecules to form the extended framework structures. Less common are one-dimensional chains of Ln polyhedra which are in turn crosslinked to form framework topologies.

We are concerned with understanding the principles of what factors influence the dimensionality of the Ln building units of

these MOFs and, as such, have decided to explore the current limit of aliphatic chain length that can be incorporated into these structures. For this effort, we have used sebacic acid ($\text{C}_{10}\text{H}_{18}\text{O}_4$), a flexible aliphatic dicarboxylic acid that is longer than previously reported for Ln-MOFs. This publication presents the synthesis, structure and thermal properties of the title compound, $[\text{Nd}(\text{C}_{10}\text{H}_{16}\text{O}_4)(\text{C}_{10}\text{H}_{16}\text{O}_3\text{OH})(\text{H}_2\text{O})]_n$, (I), a novel Ln-MOF with the longest aliphatic chain length to date.

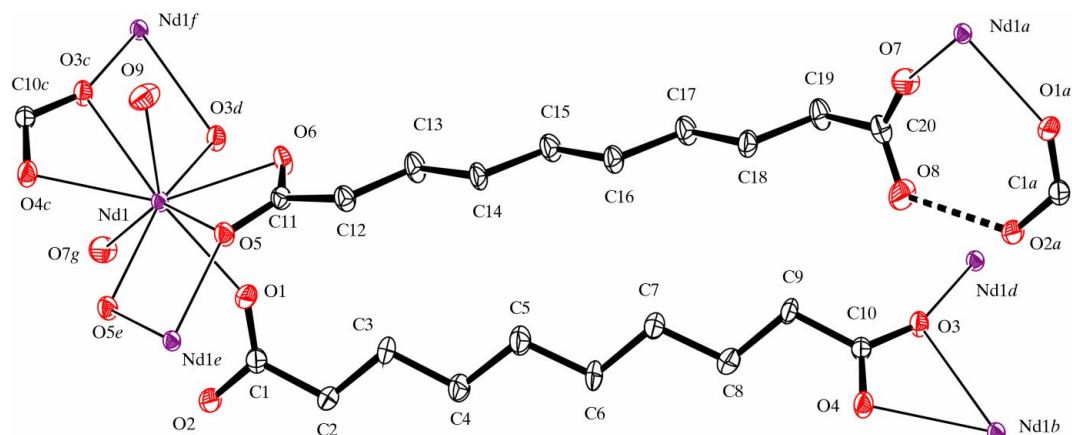


(I)

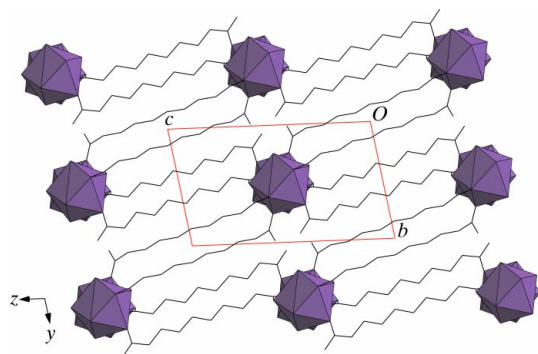
The structure of (I) contains a single crystallographically unique Nd site, within the coordination sphere of which there are two modes of bonding for the carboxylic acid (Fig. 1): each carboxylic acid chain acts as a monodentate ligand at one end and a bridging tridentate ligand at the other. There is a bound water molecule (O9) at a distance of 2.535 (5) Å from the Nd center. Two of the O atoms (O3 and O5) are involved in the edge-sharing of the $\text{NdO}_8(\text{H}_2\text{O})$ polyhedra (Table 1). These O atoms, with their respective pairs (O4 and O6), form the bridging tridentate end of each acid. The remaining two O atoms in the coordination sphere are O1 and O7. Carboxyl atoms O2 and O8 are not coordinated to Nd but are linked *via* an O—H...O hydrogen bond (Table 2).

In the crystal structure of (I), there are edge-shared chains of $\text{NdO}_8(\text{H}_2\text{O})$ tricapped trigonal prisms that propagate in the [100] direction (Fig. 2). The edge sharing results from a polymerization of Nd^{3+} centers through bridging tridentate carboxylate groups on the sebacic acid molecules. The overall topology is thus a three-dimensional framework, as these chains are then crosslinked to each other by the difunctional acid groups.

One interesting aspect of Ln-MOFs is their thermal stability and retention of crystallinity once dehydrated (Reineke *et al.*, 1999). Thermogravimetric analysis of (I) reveals a weight loss of approximately 3% between 383 and 423 K (dehydration; loss of bound H_2O group), followed by the complete breakdown of the structure beginning at 478 K. When compared with other Ln-MOFs, (I) appears to be less robust, presumably as a result of the acid chain length. Brzyska & Ozga (1991) have reported that Ln–sebacic acid complexes are stable up to approximately 553 K, but the structures of these compounds were not reported. Despite a low decomposition temperature, compound (I) does retain its crystalline structure upon dehydration at 423 K, as noted by a very similar powder diffraction pattern of the dehydrated material. The absence of H_2O (O9) was confirmed by IR spectroscopy.



The asymmetric unit of (I), together with some symmetry-equivalent atoms shown to complete the coordination sphere of the Nd atom. H atoms are not shown. Atoms labelled with the suffixes *a*–*g* are at the symmetry positions $(x - 1, y - 1, z - 1)$, $(x - 1, y, z - 1)$, $(x + 1, y, z + 1)$, $(1 - x, 1 - y, -z)$, $(1 - x, 1 - y, 1 - z)$, $(2 - x, 1 - y, 1 - z)$ and $(1 + x, 1 + y, 1 + z)$, respectively.



A polyhedral representation of (I), shown down [100]. The polyhedra are chains of edge-shared $\text{NdO}_8(\text{H}_2\text{O})$ tricapped trigonal prisms and the black lines are the linking sebacic acid backbones. The unit cell of (I) is highlighted in the center. A framework is realised when parallel chains of polyhedra are crosslinked by the sebacic acid ligands.

Several other structural features of (I) are of particular importance. For example, it is not common to observe a monodentate carboxylic acid ligand coordinated to a lanthanide center (Ouchi *et al.*, 1988). A possible explanation as to why monodentate ligands are observed in (I) is the length of the acid. Even though the acid backbone is flexible, the chain length likely hampers its ability to ‘fold in’ and become bi- or bridging tridentate, as seen in Ln-MOFs with shorter aliphatic chain lengths. Also of note is that the bound water molecule (O9) participates in a hydrogen-bonding scheme with atoms O2 and O8, which may be considered as an additional mode of connectivity between parallel $\text{NdO}_8(\text{H}_2\text{O})$ chains.

The packing of the acid chains in (I) closely resembles that of the acid molecules in pure crystalline sebacic acid (Bond *et al.*, 2001). One noticeable difference is that in (I), alternating pairs of acid chains are rotated approximately 90° about the *z* crystallographic direction. Given this arrangement, it is conceivable that the geometry and disposition of the acid

molecules have influenced the overall topology of (I), in that the Nd centers are assembled into a one-dimensional arrangement based on the location of the functional groups. Furthermore, it has been reported (Thalladi *et al.*, 2000) that dibasic aliphatic chains with an even number of C atoms form ‘layers’ in the solid state, due to the interactions of the methylene groups of neighboring acid chains. A similar assembly mechanism could be at work in the present system, in that a primary sebacic acid structure forms first, followed by Nd³⁺ centers filling in at the carboxylic acid ends of the chains.

Experimental

Neodymium(III) nitrate hexahydrate and sebacic acid are available commercially and were used without any further purification. Neodymium(III) nitrate hexahydrate (0.271 g) and sebacic acid ($\text{C}_{10}\text{H}_{18}\text{O}_4$, 0.071 g) were dissolved in water (1.36 g) in the presence of concentrated ammonium hydroxide (0.07 g). The solution (pH = 7.38) was prepared in a 23 ml Teflon-lined Parr bomb and then heated statically at 393 K for 3 d. Light-purple crystals formed *in situ* (90% yield based on Nd) and were insoluble in water, ethanol and acetone. Phase purity was confirmed by comparison of the observed and calculated powder X-ray diffraction patterns (*JADE*; Materials Data, 2003). Elemental analysis (Galbraith Laboratories, Knoxville, Tennessee, USA) of (I) confirmed the contents of the structure [observed (calculated): C 42.84% (42.61%) and H 6.55% (6.27%)].

Crystal data

[Nd(C₁₀H₁₆O₄)(C₁₀H₁₇O₄)(H₂O)]
M_r = 563.72
 Triclinic, *P* $\bar{1}$
a = 8.4365 (5) Å
b = 9.0109 (7) Å
c = 15.4080 (13) Å
 α = 97.991 (2)°
 β = 100.883 (2)°
 γ = 97.866 (2)°
V = 1122.95 (14) Å³
Z = 2

$D_x = 1.667 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1466
reflections
 $\theta = 2.3\text{--}21.5^\circ$
 $\mu = 2.36 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
Blade, purple
 $0.13 \times 0.07 \times 0.04 \text{ mm}$

Data collection

Bruker APEX CCD area-detector diffractometer	5314 independent reflections
ω and φ scans	4396 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (<i>SADABS</i> ; Sheldrick, 2002)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.820$, $T_{\text{max}} = 0.910$	$\theta_{\text{max}} = 27.9^\circ$
9349 measured reflections	$h = -11 \rightarrow 4$
	$k = -11 \rightarrow 11$
	$l = -19 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5314 reflections	$\Delta\rho_{\text{max}} = 1.14 \text{ e } \text{\AA}^{-3}$
272 parameters	$\Delta\rho_{\text{min}} = -1.68 \text{ e } \text{\AA}^{-3}$

Table 1

Selected interatomic distances (Å).

Nd1—O3 ⁱ	2.414 (4)	Nd1—O9	2.535 (5)
Nd1—O1	2.426 (4)	Nd1—O6	2.542 (4)
Nd1—O7 ⁱⁱ	2.429 (5)	Nd1—O5	2.586 (4)
Nd1—O5 ⁱⁱⁱ	2.453 (4)	Nd1—O3 ^{iv}	2.643 (4)
Nd1—O4 ^{iv}	2.509 (4)		

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1+x, 1+y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $1+x, y, 1+z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H8 \cdots O2 ⁱ	0.82	1.70	2.454 (7)	152

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

H atoms bonded to C atoms were treated as riding atoms, with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Atom H8 of the hydroxy group was visible in a difference map and was allowed for in the refinement with O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O8})$. The water atom O9 makes a number of possible hydrogen-bond contacts with nearby O atoms, but as no unambiguous locations for the water H atoms could be determined, their contributions were not included in the final refinement cycles.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve

structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (CrystalMaker Software, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1733). Services for accessing these data are described at the back of the journal.

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