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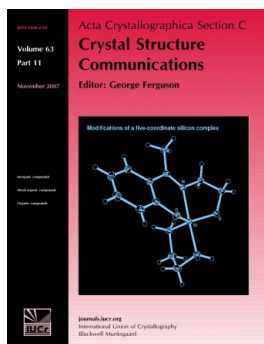
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# A dense hydrogen-bonding network and an unusually large packing index in triaquatris(2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylato)-neodymium(III) trihydrate

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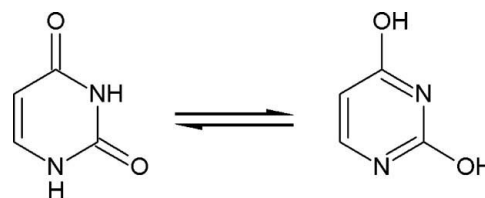
The title mononuclear complex,  $[\text{Nd}(\text{C}_5\text{H}_3\text{N}_2\text{O}_3)_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ , consists of an  $\text{Nd}^{\text{III}}$  cation, three 2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate ligands and three aqua ligands forming the neutral complex molecule, and three solvent water molecules. The pyrimidinecarboxylate ligands act in a chelating manner, *via* carboxylate and keto O atoms. The  $\text{NdO}_9$  coordination polyhedron is in the form of a distorted monocapped square antiprism. The availability of numerous hydrogen-bonding donors and acceptors results in a very dense hydrogen-bonding network, the immediate effect of which is an unusually large packing index.

**Keywords:** crystal structure; mononuclear neodymium complex; complex hydrogen-bonding network; densely packed structure.

## 1. Introduction

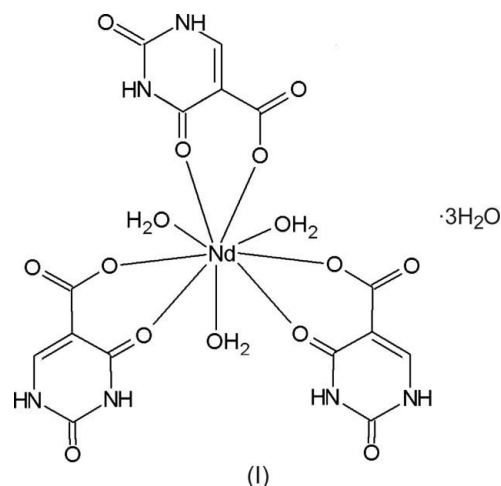
Uracil is a naturally occurring pyrimidine derivative, one of the four common nucleobases in RNA, and as such a fundamental molecule in living systems. From an electronic point of view, the molecule is non-aromatic, and thus it may undergo amide  $\leftrightarrow$  imidic acid tautomeric shifts (see Scheme 1) because any eventual nuclear instability which the molecule may have from the lack of formal aromaticity can be compensated by the cyclic amidic stability (Brown *et al.*, 1994). The amide tautomer is referred to as the lactam form, while the imidic acid tautomer is referred to as the lactim form. Of these tautomeric forms predominant at pH 7, the lactam structure is the most common form of uracil. The molecule, as well as many of its derivatives, has been used in metal–organic chemistry as an efficient ligand, though its most conspicuous

interaction ability is probably the notable tendency for hydrogen bonding, which it displays indiscriminately as both a donor and an acceptor. Most of these connectivity properties are shared, sometimes in an enhanced fashion, by many uracil derivatives, in particular the one attracting our current attention, 2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid. A search of the Cambridge Structural Database (CSD, Version 5.1; Allen, 2002) showed that the molecule displays good ligand capabilities towards alkaline metals, transition



Scheme 1

metals, lanthanides *etc.*, adapting its electronic structure to the environmental requirements. Thus, it can bind in some of its many lactam forms [either with a formal charge of  $-1$ , as in form (a) in Fig. 1, or with a formal charge of  $-2$  as in forms (b), (c) and (d) in Fig. 1], or in some of the transformed (lactim) species with a formal charge of  $-2$  [forms (e) and (f) in Fig. 1]. A curious aspect regarding all of the  $\text{Ln}^{\text{III}}$  complexes of uracil-5-carboxylate (hereinafter uc) reported to date is that uc is the sole anion present and the metal-to-ligand stoichiometry is either 1:2 or 1:2.5, meaning that the uc entities must have different  $-1$  and  $-2$  tautomeric forms in order to achieve charge balance. We present herein a simpler case, the title  $\text{Nd}^{\text{III}}$  complex, formulated as  $[\text{Nd}^{\text{III}}(\text{uc})_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ , (I) (see Scheme 2), where the metal-to-ligand ratio is 1:3, and accordingly all three coordinated  $\text{uc}^{-1}$  ligands adopt the same lactam form.



Scheme 2

## 2. Experimental

### 2.1. Synthesis and crystallization

An aqueous solution (20 ml) of  $\text{Nd}_2\text{O}_3$  (1 mmol, 0.336 g) was mixed with a water–ethanol solution (100 ml, 1:5 *v/v*)

**Table 1**

Experimental details.

Crystal data	
Chemical formula	[Nd(C <sub>5</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ].3H <sub>2</sub> O
<i>M<sub>r</sub></i>	717.62
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub>
Temperature (K)	297
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.7298 (4), 11.4266 (7), 15.2522 (10)
$\beta$ (°)	102.292 (1)
<i>V</i> (Å <sup>3</sup> )	1145.99 (12)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.37
Crystal size (mm)	0.30 × 0.24 × 0.02
Data collection	
Diffractometer	Bruker SMART CCD area-detector diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> in <i>SAINT-NT</i> ; Bruker, 2002)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.60, 0.86
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	9637, 4879, 4662
<i>R</i> <sub>int</sub>	0.023
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.661
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.021, 0.047, 0.99
No. of reflections	4879
No. of parameters	397
No. of restraints	24
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.16, -0.45
Absolute structure	Flack (1983), with 2184 Friedel pairs
Absolute structure parameter	0.002 (8)

Computer programs: *SMART* (Bruker, 2002), *SAINT* (Bruker, 2002), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

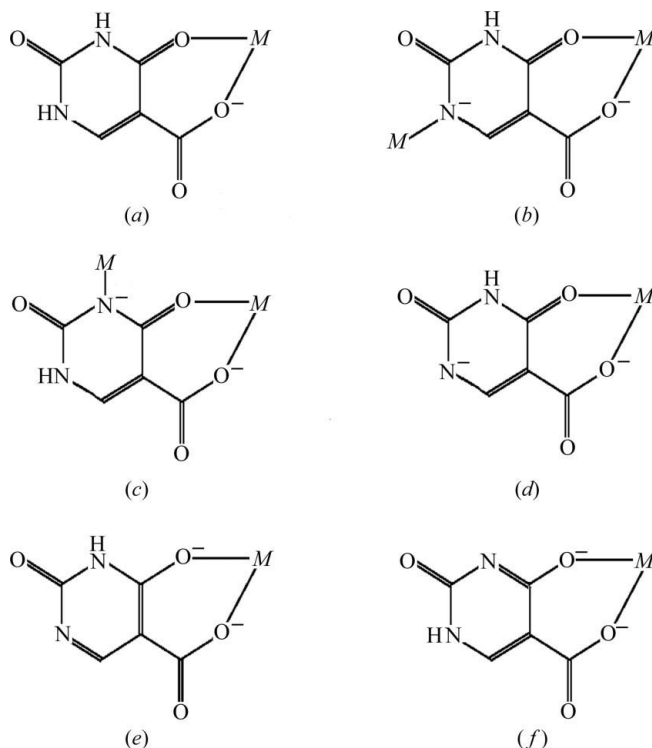
containing 2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylic acid (6 mmol, 0.9366 g) and NaOH (6 mmol, 0.24 g). The resulting solution was refluxed for 24 h and then filtered to remove the small amount of insoluble material. Single crystals of (I) suitable for X-ray diffraction studies were obtained by slow evaporation of the filtered solution.

## 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were found in a difference Fourier map, but were treated differently in the refinement. Water H atoms were refined with restrained distances [O—H = 0.85 (1) Å], and some inter-H-atom anti-bumping restraints were needed to keep a reasonable geometry. The remaining H atoms were further idealized (C—H = 0.93 Å and N—H = 0.86 Å) and allowed to ride. Displacement parameters were taken as  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{host})$ .

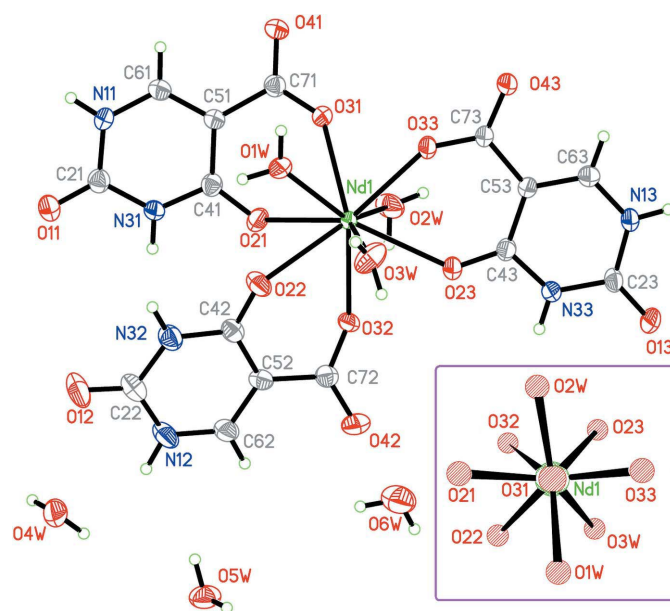
## 3. Results and discussion

The asymmetric unit of (I) (Fig. 2) consists of an Nd<sup>III</sup> cation, three uc<sup>-1</sup> anions and three aqua ligands determining the neutral complex, as well as three solvent water molecules. The three uc<sup>-1</sup> anions (distinguished by their suffixes, *i.e.* 1, 2 or 3)

**Figure 1**

The different tautomeric forms and binding modes to Tr (transition metals) and Ln (lanthanides) of uracil-5-carboxylate (uc), illustrated by some selected examples. The associated CSD refcodes and references are as follows: (a) AFEDOF (Xing *et al.*, 2007); (b) JAMROF (Sun & Jin, 2004b); (c) TAZRER (Hueso-Urena *et al.*, 1996); (d) JAMSAS (Sun & Jin, 2004b); (e) BOFTOG (Xiong *et al.*, 2008); (f) JIRNUU (Chen *et al.*, 2007).

act in a chelating manner *via* a carboxylate and a keto O atom, with Nd—O bond lengths in the ranges Nd—O<sub>keto</sub> = 2.408 (2)–

**Figure 2**

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The inset shows the NdO<sub>9</sub> coordination polyhedron.

**Table 2**  
 Selected bond lengths (Å).

Nd1—O32	2.408 (2)	Nd1—O1W	2.507 (2)
Nd1—O33	2.431 (2)	Nd1—O22	2.516 (2)
Nd1—O31	2.443 (2)	Nd1—O21	2.548 (2)
Nd1—O23	2.469 (2)	Nd1—O3W	2.541 (2)
Nd1—O2W	2.506 (2)		

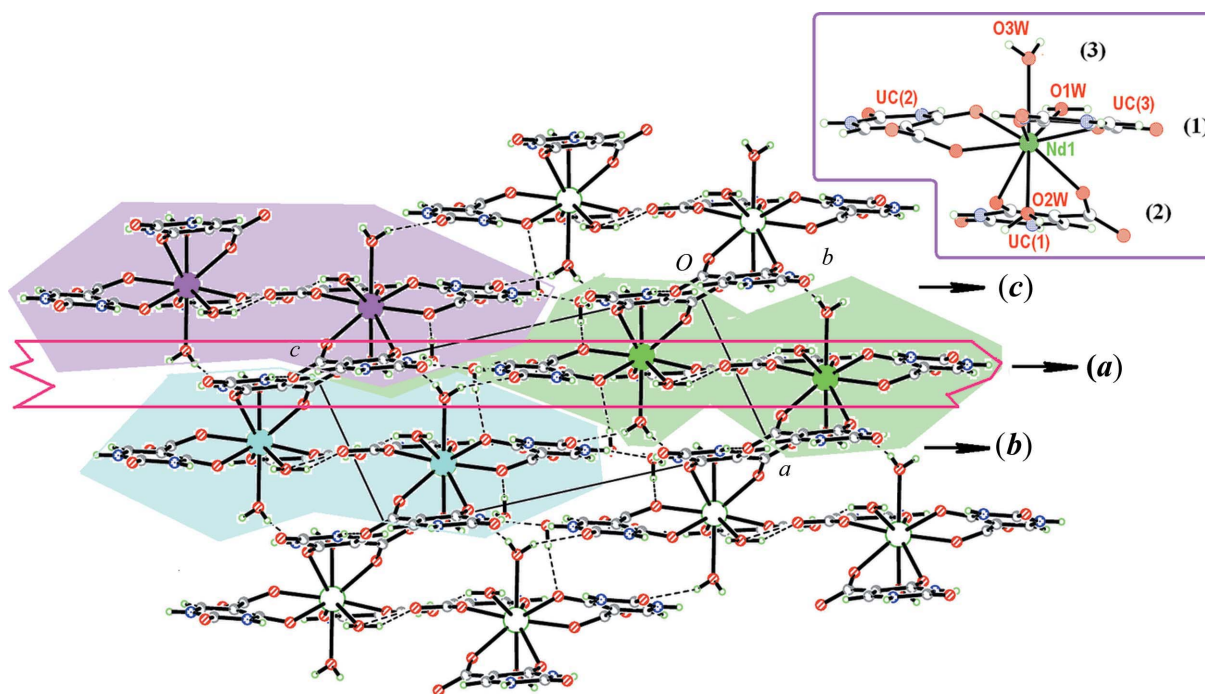
2.443 (2) Å, Nd—O<sub>carboxylate</sub> = 2.469 (2)–2.548 (2) Å and Nd—O<sub>water</sub> = 2.506 (2)–2.541 (2) Å (Table 2). These O atoms define a nine-coordination polyhedron around atom Nd1 in the form of a distorted monocapped square antiprism, having atoms O22, O32, O23 and O3W at the lower base, atoms O21, O33, O1W and O2W at the upper one, and atom O31 at the capping position (see inset in Fig. 2).

There are only two further Ln<sup>III</sup> structures having uracil anions and water molecules as coordinating groups, with no extra ancillary ligands: the Tb and Yb isomorphous complexes reported by Sun & Jin (2004*a*), hereinafter (II) and (III), respectively, formulated as [Ln<sup>III</sup>(uc<sup>-1</sup>)(uc<sup>-2</sup>)(H<sub>2</sub>O)<sub>4</sub>] and thus characterized by two coordinating uc units of different anionic nature. There are obvious differences from (I), formulated as [Nd<sup>III</sup>(uc<sup>-1</sup>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>], with three similar anions. These differences are due to the so-called ‘lanthanide contraction’ effect and derive from the different positions which these Ln cations occupy in the Ln row (Nd: smaller *Z* → larger radius → nine-coordination; Tb and Yb: larger *Z* → smaller radius → eight-coordination). As already stated, a consequence of the 1:2 Ln–anion ratio in (II) and (III) is the different anionic state (–1 and –2) which the two anions must

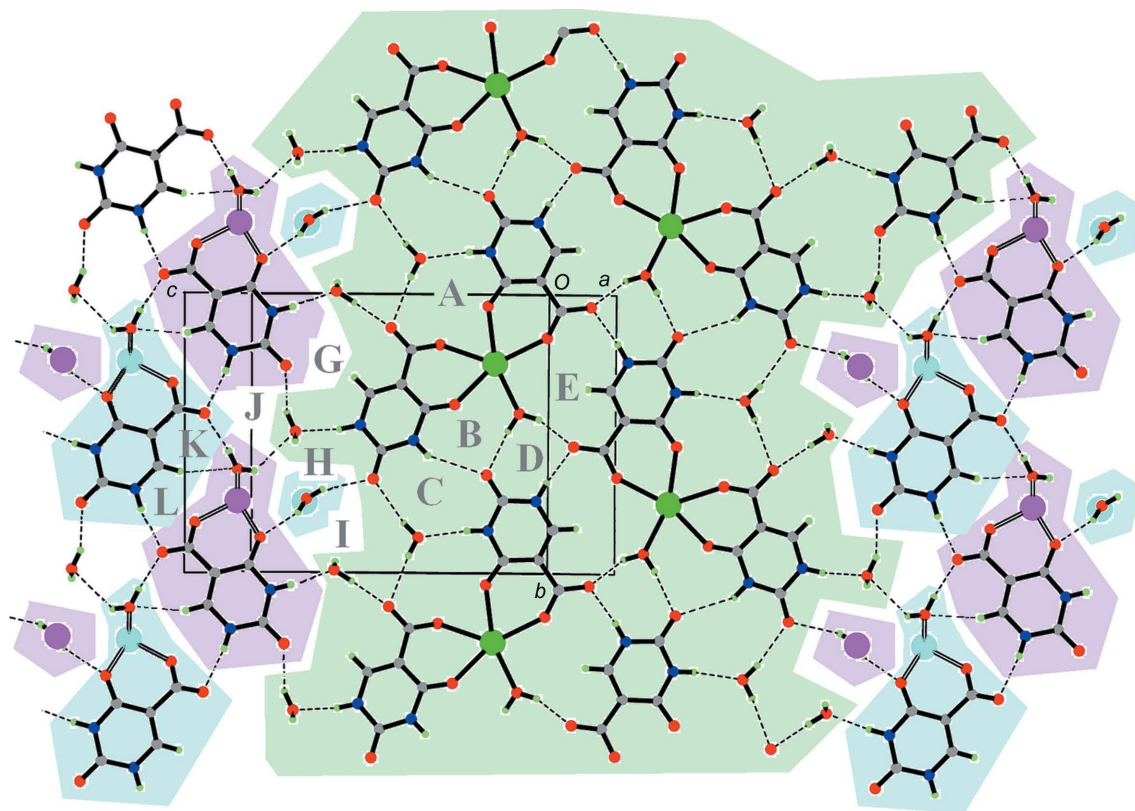
have in order to achieve charge balance, while the three anions in (I) are similarly charged (–1). Regarding their internal geometries, the three independent anions in (I) are, as expected, extremely similar to each other, while comparison with the remaining two is impaired by the fact that the uc<sup>-1</sup> and uc<sup>-2</sup> units in (II) and (III) appear disordered around a twofold axis and thus present only an average structure, obscuring any potential differences in geometry.

As expected, the rather featureless monomeric character of (I) is largely compensated by the intricate hydrogen-bonding organization it gives rise to. The dense hydrogen-bonding network has all the available N–H and O–H H atoms, plus one C–H group, as donors (19 in all) and all noncoordinated carboxylate, keto and solvent water O atoms as acceptors, complemented by a minor group of coordinated O atoms (O21, O22 and O32) and one aqua O atom (O2W) (Table 3).

The complex three-dimensional structure of (I) is favoured by a particular disposition of the ligands, best described by the inset in Fig. 3: coordination polyhedra build up in such a way as to have the Nd1—O3W bond almost perpendicular to the (201) plane (angle between bond and plane normal = 3°). Taking the Nd1 position as a reference, three different ‘atomic levels’ can be defined: the more or less planar structure at the origin, formed by the Nd1 cation and the uc(2), uc(3) and O1W units [labelled (1) in the inset], another one below, defined by the uc(1) and O2W units [labelled (2)] and an upper one, represented by O3W [labelled (3)]. In the assembly, the molecules embed into one another, mixing these three different substructures which come from entities at different levels, to define broad and more or less planar hydrogen-


**Figure 3**

A projection of the structure of (I) down [010], showing (sideways) the [102] traces of the (201) slabs. Different molecular levels have been coloured and labelled (see §3 for details). Dashed lines indicate hydrogen bonds. The inset shows the different subunits in the coordination polyhedron which make up the slabs.



**Figure 4**

A view of slab (a), at right angles to the orientation in Fig. 3, showing the large number of loops arising from the 'in-plane' hydrogen-bonding interactions (dashed lines). Graph-set codes: **A**  $R_2^2(10)$ , **B**  $R_2^1(8)$ , **C**  $R_3^3(10)$ , **D**  $R_3^2(8)$ , **E**  $R_2^2(12)$ , **G**  $R_4^4(14)$ , **H**  $R_4^4(12)$ , **I**  $R_6^6(14)$ , **J**  $R_2^2(10)$ , **K**  $R_2^2(7)$  and **L**  $R_2^2(9)$ . [For a survey of graph-set nomenclature of hydrogen-bonding loops, see Bernstein *et al.* (1995).]

bonded slabs parallel to (201) [mean deviation from the least-squares plane defined by the C, N and O atoms = 0.35 Å; maximum deviation =  $\pm 1.20$  Å for atom O31; separation between slabs = 3.075 Å, *viz.* the (201) spacing].

**Table 3**

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ... <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> — <i>H</i> ... <i>A</i>
O1W—H1WA...O43 <sup>i</sup>	0.85 (3)	1.93 (3)	2.692 (3)	150 (4)
O1W—H1WB...O13 <sup>ii</sup>	0.85 (2)	2.02 (2)	2.860 (3)	170 (3)
O2W—H2WA...O41 <sup>iii</sup>	0.85 (2)	1.83 (2)	2.670 (3)	169 (3)
O2W—H2WB...O4W <sup>iv</sup>	0.85 (2)	2.41 (2)	2.852 (4)	113 (2)
O3W—H3WA...O21 <sup>v</sup>	0.83 (4)	2.25 (4)	3.048 (4)	160 (4)
O3W—H3WB...O12 <sup>vi</sup>	0.84 (2)	2.19 (2)	2.964 (4)	155 (3)
O4W—H4WA...O11	0.86 (2)	1.98 (2)	2.745 (4)	148 (3)
O4W—H4WB...O32 <sup>vii</sup>	0.85 (3)	2.05 (3)	2.822 (3)	149 (3)
O5W—H5WA...O42	0.85 (4)	1.85 (4)	2.703 (4)	175 (4)
O5W—H5WB...O22 <sup>viii</sup>	0.85 (2)	2.15 (2)	2.999 (4)	173 (2)
O6W—H6WA...O12 <sup>ix</sup>	0.85 (4)	2.22 (3)	3.026 (4)	159 (4)
O6W—H6WB...O42	0.84 (3)	2.25 (3)	3.083 (4)	170 (4)
N11—H11...O41 <sup>x</sup>	0.86	1.97	2.817 (3)	170
N31—H31...O5W <sup>vii</sup>	0.86	1.90	2.756 (4)	171
N12—H12...O4W	0.86	1.85	2.698 (4)	168
N32—H32...O13 <sup>ii</sup>	0.86	2.54	3.312 (4)	150
N13—H13...O43 <sup>x</sup>	0.86	1.88	2.733 (5)	172
N33—H33...O6W	0.86	2.04	2.888 (4)	169
C61—H61...O2W <sup>ix</sup>	0.93	2.39	3.285 (4)	161

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

Fig. 3 presents a projection down [010], showing (sideways) the [10 $\bar{2}$ ] traces of these arrays. For convenience, we have labelled some of them as (a) (enclosed between horizontal red lines; colours refer to the electronic version of the journal), (b) and (c). Molecules with their Nd<sup>III</sup> cations occupying structure (a) have been coloured green, those in (b) cyan and those in (c) magenta. It is clear that the (mostly green) slab at (a) receives contributions from molecules at upper (c) and lower (b) levels. This can be better visualized by inspection of Fig. 4, which presents a view of slab (a) rotated along a horizontal line, in a projection down the normal to the plane. Eleven different hydrogen-bonding loops can be seen in the plane (see caption to Fig. 4 for loop details), resulting from 17 different hydrogen bonds out of the 19 listed in Table 3.

The central part of Fig. 4 (green in the electronic version of the paper), running along [010], is made up of type (1) substructures containing Nd<sup>III</sup> cations, two uc units and one aqua ligand, as well as most of the solvent water molecules; loops A–E serve to link these 'in-plane' molecules internally. The remaining loops (G–L) mix the central part with type (2) and type (3) subunits from molecules in upper or lower levels, and complete the lateral connectivity along [10 $\bar{2}$ ] of these broad planar structures.

Connection between slabs is achieved by covalent bonds involving Nd<sup>III</sup> cations bound to type (2) and (3) substructures, plus the two remaining hydrogen bonds involving atoms

H4WB and H5WB (eighth and tenth entries in Table 3), not involved in the in-plane pattern.

The effect of this dense interactive network can be assessed both by the rather large calculated density ( $2.08 \text{ Mg m}^{-3}$ ), which lies in the 15th highest percentile of about 1000 Nd complexes having C, N, O and H in their structures, and by the large packing index of 77.7% [as calculated by *PLATON* (Spek, 2009), following Kitajgorodskij (1973)], appreciably larger than average (*ca* 65%; *PLATON* web page, <http://www.cryst.chem.uu.nl/platon/>).

There are not many reported  $\text{Ln}^{\text{III}}$  complexes with uc ligands (ten in all, divided into just three different structural types), and none with a 1:3 Ln–uc ratio. One structural type is the group consisting of structures (II) and (III) (discussed above), bearing no ancillary ligands except aqua. There are two further structural types, one with phenanthroline as an ancillary ligand, the first formulated as  $[\text{Ln}^{\text{III}}(\text{uc}^{-1})(\text{uc}^{-2})(\text{phen})_2]$  (phen is 1,10-phenanthroline), with six isomorphous structures reported [Ln = Eu, Tb and Yb (Sun & Jin, 2004a), Gd (Xiong *et al.*, 2008), Er (Xing *et al.*, 2008a) and Dy (Liu *et al.*, 2009)], and the second formulated as  $[\text{Ln}^{\text{III}}_2(\text{uc}^{-1})_4(\text{uc}^{-2})(\text{phen})_4]$ , with two isomorphous structures [Ln = Pr (Sun & Jin, 2004a) and Nd (Xing *et al.*, 2008b)]. All of them present a mixture of  $\text{uc}^{-1}$  and  $\text{uc}^{-2}$  ligands, and their packing indices (in the range 75–77%) are similar to that found for (I) (77.7%), thus confirming the strong cohesion capabilities of the uc group in all the structures in which it takes part.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3083). Services for accessing these data are described at the back of the journal.

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## supplementary materials

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## A dense hydrogen-bonding network and an unusually large packing index in triaquatris(2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylato)neodymium(III) trihydrate

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### Computing details

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### Triaquatris(2,4-dioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylato)neodymium(III) trihydrate

#### Crystal data

[Nd(C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>O<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]·3H<sub>2</sub>O

$M_r = 717.62$

Monoclinic,  $P2_1$

Hall symbol: P 2yb

$a = 6.7298$  (4) Å

$b = 11.4266$  (7) Å

$c = 15.2522$  (10) Å

$\beta = 102.292$  (1)°

$V = 1145.99$  (12) Å<sup>3</sup>

$Z = 2$

$F(000) = 714$

$D_x = 2.080$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 7791 reflections

$\theta = 2.2$ – $28.0^\circ$

$\mu = 2.37$  mm<sup>-1</sup>

$T = 297$  K

Plates, colourless

$0.30 \times 0.24 \times 0.02$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

CCD rotation images, thin slices scans

Absorption correction: multi-scan (*SADABS* in *SAINTE-NT*; Bruker, 2002)

$T_{\min} = 0.60$ ,  $T_{\max} = 0.86$

9637 measured reflections

4879 independent reflections

4662 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 28.0^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -8 \rightarrow 8$

$k = -14 \rightarrow 15$

$l = -20 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.047$

$S = 0.99$

4879 reflections

397 parameters

24 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent

and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.003$$

$$\Delta\rho_{\max} = 1.16 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), with 2184

Friedel pairs

Absolute structure parameter: 0.002 (8)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Nd1	0.67842 (2)	0.748313 (19)	0.793202 (8)	0.01921 (5)
O11	1.0954 (4)	1.2593 (3)	0.73928 (15)	0.0362 (6)
O21	0.9821 (4)	0.8787 (2)	0.78671 (16)	0.0281 (5)
O31	0.8422 (4)	0.82674 (19)	0.93980 (15)	0.0262 (5)
O41	0.9857 (4)	0.9356 (2)	1.05466 (16)	0.0314 (6)
N11	1.0341 (4)	1.2087 (2)	0.87545 (18)	0.0256 (6)
H11	1.0400	1.2802	0.8933	0.031*
C21	1.0620 (5)	1.1843 (3)	0.7910 (2)	0.0257 (7)
N31	1.0518 (4)	1.0674 (2)	0.76917 (18)	0.0245 (6)
H31	1.0803	1.0484	0.7187	0.029*
C41	1.0008 (5)	0.9788 (3)	0.8200 (2)	0.0235 (7)
C51	0.9760 (5)	1.0094 (3)	0.9086 (2)	0.0223 (7)
C61	0.9975 (5)	1.1234 (3)	0.9316 (2)	0.0251 (7)
H61	0.9865	1.1447	0.9893	0.030*
C71	0.9326 (5)	0.9186 (3)	0.9724 (2)	0.0236 (7)
O12	0.7256 (4)	1.1643 (2)	0.4699 (2)	0.0472 (7)
O22	0.5974 (4)	0.8954 (2)	0.66795 (16)	0.0320 (6)
O32	0.7972 (4)	0.68192 (18)	0.66353 (15)	0.0270 (5)
O42	0.7745 (5)	0.6217 (2)	0.52428 (19)	0.0428 (7)
N12	0.7857 (5)	0.9715 (3)	0.4441 (2)	0.0359 (8)
H12	0.8162	0.9873	0.3934	0.043*
C22	0.7277 (5)	1.0615 (3)	0.4929 (3)	0.0334 (8)
N32	0.6712 (5)	1.0252 (3)	0.5698 (2)	0.0315 (7)
H32	0.6325	1.0788	0.6020	0.038*
C42	0.6700 (5)	0.9120 (3)	0.6009 (2)	0.0250 (7)
C52	0.7458 (6)	0.8250 (3)	0.5497 (3)	0.0254 (8)
C62	0.7971 (5)	0.8582 (3)	0.4726 (2)	0.0295 (8)
H62	0.8419	0.8016	0.4375	0.035*
C72	0.7726 (6)	0.6999 (3)	0.5797 (3)	0.0244 (8)
O13	0.5735 (5)	0.1474 (2)	0.7530 (2)	0.0328 (8)
O23	0.5926 (4)	0.5414 (2)	0.75681 (17)	0.0366 (6)
O33	0.5346 (4)	0.65505 (19)	0.90886 (17)	0.0335 (6)
O43	0.4803 (4)	0.54424 (19)	1.01893 (16)	0.0341 (6)
N13	0.5264 (3)	0.2410 (4)	0.87985 (16)	0.0252 (5)
H13	0.5174	0.1758	0.9069	0.030*



C23	0.5580 (4)	0.2385 (4)	0.79405 (19)	0.0234 (6)
N33	0.5765 (6)	0.3467 (3)	0.7582 (2)	0.0245 (8)
H33	0.5970	0.3483	0.7044	0.029*
C43	0.5657 (5)	0.4533 (3)	0.7992 (2)	0.0236 (7)
C53	0.5263 (5)	0.4490 (3)	0.8883 (2)	0.0219 (7)
C63	0.5089 (5)	0.3421 (3)	0.9238 (2)	0.0252 (7)
H63	0.4837	0.3378	0.9814	0.030*
C73	0.5127 (5)	0.5568 (3)	0.9421 (2)	0.0218 (7)
O1W	0.4896 (4)	0.92668 (19)	0.82582 (16)	0.0294 (5)
H1WA	0.462 (6)	0.948 (3)	0.8750 (13)	0.035*
H1WB	0.506 (6)	0.9892 (18)	0.798 (2)	0.035*
O2W	0.9973 (4)	0.6349 (2)	0.85270 (18)	0.0380 (6)
H2WA	1.019 (5)	0.5706 (14)	0.8814 (15)	0.046*
H2WB	1.094 (3)	0.6403 (16)	0.8250 (12)	0.046*
O3W	0.3033 (3)	0.7379 (5)	0.71871 (17)	0.0447 (8)
H3WA	0.217 (5)	0.787 (3)	0.726 (3)	0.054*
H3WB	0.264 (6)	0.705 (3)	0.6692 (14)	0.054*
O4W	0.9236 (4)	0.9961 (2)	0.29146 (19)	0.0415 (7)
H4WA	0.959 (5)	0.9296 (17)	0.274 (3)	0.050*
H4WB	1.037 (3)	1.030 (3)	0.312 (3)	0.050*
O5W	0.8260 (4)	0.4919 (3)	0.38267 (18)	0.0407 (6)
H5WA	0.816 (6)	0.531 (4)	0.429 (2)	0.049*
H5WB	0.709 (3)	0.462 (3)	0.364 (2)	0.049*
O6W	0.6925 (5)	0.3735 (3)	0.5876 (2)	0.0530 (8)
H6WA	0.734 (7)	0.322 (2)	0.556 (3)	0.064*
H6WB	0.704 (8)	0.4391 (17)	0.564 (3)	0.064*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Nd1	0.02867 (8)	0.01333 (7)	0.01710 (7)	-0.00035 (10)	0.00821 (5)	-0.00010 (9)
O11	0.0538 (13)	0.0248 (14)	0.0337 (12)	-0.0022 (15)	0.0174 (10)	0.0036 (15)
O21	0.0369 (14)	0.0220 (11)	0.0281 (13)	-0.0071 (10)	0.0131 (11)	-0.0057 (10)
O31	0.0374 (13)	0.0203 (11)	0.0195 (12)	-0.0051 (10)	0.0031 (10)	-0.0004 (9)
O41	0.0452 (16)	0.0299 (14)	0.0171 (14)	-0.0047 (13)	0.0025 (11)	0.0016 (12)
N11	0.0341 (15)	0.0177 (12)	0.0259 (14)	-0.0040 (11)	0.0083 (12)	-0.0024 (10)
C21	0.0263 (17)	0.0234 (17)	0.0268 (18)	0.0007 (14)	0.0040 (14)	0.0013 (14)
N31	0.0348 (15)	0.0203 (13)	0.0211 (14)	0.0000 (12)	0.0121 (12)	-0.0006 (11)
C41	0.0213 (16)	0.0237 (16)	0.0259 (17)	-0.0025 (13)	0.0060 (13)	0.0001 (13)
C51	0.0259 (17)	0.0224 (17)	0.0181 (17)	-0.0016 (14)	0.0037 (14)	0.0003 (13)
C61	0.0285 (18)	0.0273 (18)	0.0186 (17)	-0.0016 (15)	0.0027 (14)	0.0009 (14)
C71	0.0247 (16)	0.0221 (16)	0.0240 (17)	0.0007 (13)	0.0055 (13)	0.0009 (13)
O12	0.0586 (18)	0.0351 (14)	0.0540 (19)	0.0037 (13)	0.0255 (15)	0.0199 (13)
O22	0.0412 (14)	0.0300 (13)	0.0293 (13)	0.0092 (11)	0.0178 (11)	0.0081 (10)
O32	0.0446 (14)	0.0206 (11)	0.0186 (12)	0.0045 (10)	0.0129 (10)	0.0015 (9)
O42	0.069 (2)	0.0349 (16)	0.0267 (16)	0.0024 (14)	0.0164 (15)	-0.0085 (12)
N12	0.0427 (19)	0.0390 (18)	0.0299 (18)	0.0001 (15)	0.0167 (15)	0.0103 (14)
C22	0.0308 (19)	0.039 (2)	0.032 (2)	0.0001 (16)	0.0096 (16)	0.0118 (17)
N32	0.0377 (17)	0.0281 (16)	0.0306 (17)	0.0060 (13)	0.0115 (14)	0.0057 (13)
C42	0.0239 (16)	0.0270 (17)	0.0233 (17)	0.0003 (13)	0.0033 (13)	0.0034 (13)

C52	0.0272 (19)	0.029 (2)	0.020 (2)	0.0027 (16)	0.0044 (16)	0.0005 (16)
C62	0.0327 (19)	0.033 (2)	0.0243 (19)	-0.0040 (15)	0.0100 (16)	0.0003 (16)
C72	0.0218 (17)	0.0282 (17)	0.025 (2)	-0.0041 (14)	0.0084 (15)	-0.0011 (15)
O13	0.051 (2)	0.0154 (15)	0.035 (2)	0.0028 (15)	0.0159 (17)	-0.0020 (13)
O23	0.0673 (18)	0.0183 (11)	0.0302 (14)	-0.0073 (12)	0.0235 (13)	-0.0017 (10)
O33	0.0609 (17)	0.0165 (11)	0.0301 (14)	-0.0063 (11)	0.0253 (13)	-0.0023 (9)
O43	0.0618 (17)	0.0189 (11)	0.0268 (13)	-0.0028 (11)	0.0208 (12)	-0.0009 (10)
N13	0.0353 (12)	0.0158 (12)	0.0261 (11)	-0.0023 (16)	0.0104 (9)	0.0012 (16)
C23	0.0270 (13)	0.0170 (17)	0.0276 (14)	0.0017 (18)	0.0087 (11)	0.0041 (19)
N33	0.035 (2)	0.0190 (18)	0.022 (2)	-0.0006 (16)	0.0115 (17)	0.0001 (15)
C43	0.0279 (17)	0.0184 (15)	0.0272 (18)	-0.0016 (13)	0.0114 (14)	-0.0014 (13)
C53	0.0262 (16)	0.0181 (15)	0.0224 (17)	-0.0029 (13)	0.0073 (13)	-0.0015 (13)
C63	0.0306 (18)	0.0230 (16)	0.0243 (17)	0.0000 (14)	0.0108 (14)	-0.0013 (13)
C73	0.0276 (16)	0.0163 (15)	0.0226 (17)	-0.0023 (13)	0.0081 (13)	-0.0001 (13)
O1W	0.0435 (15)	0.0216 (11)	0.0245 (13)	0.0037 (11)	0.0105 (11)	-0.0032 (10)
O2W	0.0509 (17)	0.0316 (14)	0.0332 (16)	0.0172 (12)	0.0128 (13)	0.0087 (11)
O3W	0.0377 (13)	0.041 (2)	0.0510 (15)	-0.0081 (16)	-0.0002 (11)	-0.0173 (19)
O4W	0.0586 (18)	0.0302 (14)	0.0418 (17)	-0.0077 (13)	0.0244 (14)	-0.0016 (12)
O5W	0.0447 (16)	0.0495 (17)	0.0319 (16)	-0.0067 (13)	0.0171 (13)	-0.0105 (12)
O6W	0.062 (2)	0.061 (2)	0.0381 (18)	-0.0034 (18)	0.0178 (15)	-0.0001 (15)

*Geometric parameters (Å, °)*

Nd1—O32	2.408 (2)	N32—H32	0.8600
Nd1—O33	2.431 (2)	C42—C52	1.424 (5)
Nd1—O31	2.443 (2)	C52—C62	1.350 (5)
Nd1—O23	2.469 (2)	C52—C72	1.499 (5)
Nd1—O2W	2.506 (2)	C62—H62	0.9300
Nd1—O1W	2.507 (2)	O13—C23	1.230 (5)
Nd1—O22	2.516 (2)	O23—C43	1.231 (4)
Nd1—O21	2.548 (2)	O33—C73	1.253 (4)
Nd1—O3W	2.541 (2)	O43—C73	1.244 (4)
O11—C21	1.218 (4)	N13—C63	1.353 (5)
O21—C41	1.247 (4)	N13—C23	1.370 (4)
O31—C71	1.261 (4)	N13—H13	0.8600
O41—C71	1.244 (4)	C23—N33	1.368 (5)
N11—C61	1.354 (4)	N33—C43	1.378 (4)
N11—C21	1.370 (4)	N33—H33	0.8600
N11—H11	0.8600	C43—C53	1.440 (4)
C21—N31	1.374 (4)	C53—C63	1.352 (4)
N31—C41	1.363 (4)	C53—C73	1.494 (4)
N31—H31	0.8600	C63—H63	0.9300
C41—C51	1.439 (5)	O1W—H1WA	0.846 (10)
C51—C61	1.349 (5)	O1W—H1WB	0.848 (10)
C51—C71	1.494 (4)	O2W—H2WA	0.851 (10)
C61—H61	0.9300	O2W—H2WB	0.850 (9)
O12—C22	1.226 (4)	O3W—H3WA	0.835 (10)
O22—C42	1.238 (4)	O3W—H3WB	0.833 (10)
O32—C72	1.271 (4)	O4W—H4WA	0.855 (10)
O42—C72	1.232 (4)	O4W—H4WB	0.854 (10)

N12—C62	1.362 (5)	O5W—H5WA	0.850 (10)
N12—C22	1.374 (5)	O5W—H5WB	0.849 (10)
N12—H12	0.8600	O6W—H6WA	0.841 (10)
C22—N32	1.372 (5)	O6W—H6WB	0.842 (10)
N32—C42	1.378 (4)		
O32—Nd1—O33	135.30 (8)	C42—O22—Nd1	132.0 (2)
O32—Nd1—O31	134.69 (8)	C72—O32—Nd1	141.3 (2)
O33—Nd1—O31	70.64 (8)	C62—N12—C22	122.8 (3)
O32—Nd1—O23	67.44 (8)	C62—N12—H12	118.6
O33—Nd1—O23	68.48 (8)	C22—N12—H12	118.6
O31—Nd1—O23	126.54 (8)	O12—C22—N32	123.1 (4)
O32—Nd1—O2W	74.10 (8)	O12—C22—N12	123.4 (3)
O33—Nd1—O2W	87.31 (9)	N32—C22—N12	113.5 (3)
O31—Nd1—O2W	70.94 (8)	C22—N32—C42	127.0 (3)
O23—Nd1—O2W	74.19 (9)	C22—N32—H32	116.5
O32—Nd1—O1W	133.63 (8)	C42—N32—H32	116.5
O33—Nd1—O1W	85.15 (8)	O22—C42—N32	117.4 (3)
O31—Nd1—O1W	70.68 (8)	O22—C42—C52	126.6 (3)
O23—Nd1—O1W	135.97 (9)	N32—C42—C52	115.9 (3)
O2W—Nd1—O1W	141.23 (9)	C62—C52—C42	118.0 (3)
O32—Nd1—O22	69.09 (7)	C62—C52—C72	119.8 (4)
O33—Nd1—O22	142.03 (8)	C42—C52—C72	122.2 (3)
O31—Nd1—O22	115.63 (8)	C52—C62—N12	122.6 (4)
O23—Nd1—O22	117.81 (8)	C52—C62—H62	118.7
O2W—Nd1—O22	130.63 (9)	N12—C62—H62	118.7
O1W—Nd1—O22	64.56 (8)	O42—C72—O32	123.7 (4)
O32—Nd1—O21	75.11 (8)	O42—C72—C52	120.0 (4)
O33—Nd1—O21	136.97 (8)	O32—C72—C52	116.2 (3)
O31—Nd1—O21	67.16 (8)	C43—O23—Nd1	136.0 (2)
O23—Nd1—O21	134.62 (8)	C73—O33—Nd1	141.8 (2)
O2W—Nd1—O21	71.60 (8)	C63—N13—C23	122.6 (4)
O1W—Nd1—O21	88.68 (8)	C63—N13—H13	118.7
O22—Nd1—O21	68.03 (8)	C23—N13—H13	118.7
O32—Nd1—O3W	95.16 (9)	O13—C23—N33	122.4 (3)
O33—Nd1—O3W	78.04 (10)	O13—C23—N13	123.5 (4)
O31—Nd1—O3W	129.65 (10)	N33—C23—N13	114.1 (4)
O23—Nd1—O3W	72.06 (15)	C23—N33—C43	126.8 (3)
O2W—Nd1—O3W	146.14 (14)	C23—N33—H33	116.6
O1W—Nd1—O3W	68.26 (14)	C43—N33—H33	116.6
O22—Nd1—O3W	69.98 (12)	O23—C43—N33	117.2 (3)
O21—Nd1—O3W	137.62 (12)	O23—C43—C53	126.9 (3)
C41—O21—Nd1	122.2 (2)	N33—C43—C53	115.9 (3)
C71—O31—Nd1	138.8 (2)	C63—C53—C43	117.3 (3)
C61—N11—C21	121.9 (3)	C63—C53—C73	120.2 (3)
C61—N11—H11	119.0	C43—C53—C73	122.5 (3)
C21—N11—H11	119.0	N13—C63—C53	123.3 (3)
O11—C21—N11	123.1 (3)	N13—C63—H63	118.4
O11—C21—N31	122.3 (3)	C53—C63—H63	118.4

N11—C21—N31	114.5 (3)	O43—C73—O33	122.9 (3)
C41—N31—C21	126.1 (3)	O43—C73—C53	117.8 (3)
C41—N31—H31	116.9	O33—C73—C53	119.3 (3)
C21—N31—H31	116.9	Nd1—O1W—H1WA	129 (2)
O21—C41—N31	117.7 (3)	Nd1—O1W—H1WB	118 (2)
O21—C41—C51	125.7 (3)	H1WA—O1W—H1WB	106.0 (16)
N31—C41—C51	116.6 (3)	Nd1—O2W—H2WA	132 (2)
C61—C51—C41	116.9 (3)	Nd1—O2W—H2WB	118.0 (14)
C61—C51—C71	121.7 (3)	H2WA—O2W—H2WB	104.8 (15)
C41—C51—C71	121.4 (3)	Nd1—O3W—H3WA	124 (3)
C51—C61—N11	123.6 (3)	Nd1—O3W—H3WB	121 (3)
C51—C61—H61	118.2	H3WA—O3W—H3WB	109.0 (17)
N11—C61—H61	118.2	H4WA—O4W—H4WB	103.3 (16)
O41—C71—O31	122.6 (3)	H5WA—O5W—H5WB	105.3 (16)
O41—C71—C51	119.6 (3)	H6WA—O6W—H6WB	108.0 (17)
O31—C71—C51	117.8 (3)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ O43 <sup>i</sup>	0.85 (3)	1.93 (3)	2.692 (3)	150 (4)
O1W—H1WB $\cdots$ O13 <sup>ii</sup>	0.85 (2)	2.02 (2)	2.860 (3)	170 (3)
O2W—H2WA $\cdots$ O41 <sup>iii</sup>	0.85 (2)	1.83 (2)	2.670 (3)	169 (3)
O2W—H2WB $\cdots$ O4W <sup>iv</sup>	0.85 (2)	2.41 (2)	2.852 (4)	113 (2)
O3W—H3WA $\cdots$ O21 <sup>v</sup>	0.83 (4)	2.25 (4)	3.048 (4)	160 (4)
O3W—H3WB $\cdots$ O12 <sup>vi</sup>	0.84 (2)	2.19 (2)	2.964 (4)	155 (3)
O4W—H4WA $\cdots$ O11	0.86 (2)	1.98 (2)	2.745 (4)	148 (3)
O4W—H4WB $\cdots$ O32 <sup>vii</sup>	0.85 (3)	2.05 (3)	2.822 (3)	149 (3)
O5W—H5WA $\cdots$ O42	0.85 (4)	1.85 (4)	2.703 (4)	175 (4)
O5W—H5WB $\cdots$ O22 <sup>vi</sup>	0.85 (2)	2.15 (2)	2.999 (4)	173 (2)
O6W—H6WA $\cdots$ O12 <sup>viii</sup>	0.85 (4)	2.22 (3)	3.026 (4)	159 (4)
O6W—H6WB $\cdots$ O42	0.84 (3)	2.25 (3)	3.083 (4)	170 (4)
N11—H11 $\cdots$ O41 <sup>ix</sup>	0.86	1.97	2.817 (3)	170
N31—H31 $\cdots$ O5W <sup>vii</sup>	0.86	1.90	2.756 (4)	171
N12—H12 $\cdots$ O4W	0.86	1.85	2.698 (4)	168
N32—H32 $\cdots$ O13 <sup>ii</sup>	0.86	2.54	3.312 (4)	150
N13—H13 $\cdots$ O43 <sup>x</sup>	0.86	1.88	2.733 (5)	172
N33—H33 $\cdots$ O6W	0.86	2.04	2.888 (4)	169
C61—H61 $\cdots$ O2W <sup>ix</sup>	0.93	2.39	3.285 (4)	161

Symmetry codes: (i)  $-x+1, y+1/2, -z+2$ ; (ii)  $x, y+1, z$ ; (iii)  $-x+2, y-1/2, -z+2$ ; (iv)  $-x+2, y-1/2, -z+1$ ; (v)  $x-1, y, z$ ; (vi)  $-x+1, y-1/2, -z+1$ ; (vii)  $-x+2, y+1/2, -z+1$ ; (viii)  $x, y-1, z$ ; (ix)  $-x+2, y+1/2, -z+2$ ; (x)  $-x+1, y-1/2, -z+2$ .