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A neodymium(III)–ammonium complex involving oxalate and carbonate ligands: $(NH_4)_2[Nd_2(C_2O_4)_3(CO_3)(H_2O)]\cdot H_2O$

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The title compound, diammonium aqua-μ-carbonato-tri-μ-oxalato-dineodymium(III) hydrate, $(NH_4)_2[Nd_2(CO_3)(C_2O_4)_3(H_2O)]\cdot H_2O$, involving the two ligands oxalate and carbonate, has been prepared hydrothermally as single crystals. The Nd atoms form a tetranuclear unit across the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Starting from this tetranuclear unit, the oxalate ligands serve to develop a three-dimensional network. The carbonate group acts as a bis-chelating ligand to two Nd atoms, and is monodentate to a third Nd atom. The oxalate groups are all bis-chelating. The two independent Nd atoms are ninefold coordinated and the coordination polyhedron of these atoms is a distorted monocapped antiprism.

Comment

Among novel open-framework materials, those of lanthanide oxalates are particularly noteworthy. These oxalates present a layered honeycomb network (Ollendorf & Weigel, 1969; Hansson, 1970, 1973; Trollet *et al.*, 1997). Some mixed lanthanide–alkali metal (including the ammonium ion) oxalates also have layer structures (McDonald & Spink, 1967; Bataille *et al.*, 2000). However, the main remaining challenge is to connect the layers of these complexes *via* other ligands in order to preserve the open architecture as far as possible. To this end, carbonate has been used and novel families have been obtained, *e.g.* $[Ln(H_2O)]_2(C_2O_4)_2(CO_3)\cdot 2.5H_2O$, with Ln = Ce–Eu (Roméro *et al.*, 1996), or $[Ln(H_2O)]_2(C_2O_4)(CO_3)_2$, with Ln = Eu–Ho and Y (Roméro *et al.*, 1997; Bataille & Louër, 2000). The latter family provides a good example of an open framework; almost 15% of the unit-cell volume is empty.

Instead of carbonate, oxalate can be used as the additional ligand; $[M\mathrm{Ln}(H_2O)_n](C_2O_4)_2\cdot H_2O$, with M = Li, Ln = La–Gd and n = 1, or M = Na, Ln = Ce–Nd and n = 2 (Roméro *et al.*, 1995), $YK(C_2O_4)_2\cdot 4H_2O$ (Bataille *et al.*, 1999), $La(C_2O_4)_2\cdot NH_4$ (Trombe *et al.*, 2001), and $(C_6N_2H_{16})_{0.5}[Y(H_2O)(C_2O_4)_2]\cdot 2H_2O$ and $(C_5N_2H_{12})[Y(C_2O_4)]$ (Vaidhyanathan *et al.*, 2001) have been isolated to date.

In view of the limited number of three-dimensional mixed rare-earth oxalates with alkali metals (including ammonium and protonated organic amines), we have explored the possibility of synthesizing new examples by the hydrothermal method. Single crystals of a new ammonium–neodymium oxalate–carbonate, (I), have been isolated and its three-dimensional structure is reported here.

The cell formula of (I), $4(NH_4)^+[Nd_2(C_2O_4)_3(CO_3)(H_2O)]_2^{4-}\cdot 2H_2O$, is based on two units. The anionic species build up a three-dimensional network, in which the cationic ammonium groups and the solvate water molecule, O*W*2, are intercalated. The independent atoms are two Nd atoms, Nd1 and Nd2, two water molecules, O*W*1 and O*W*2, one carbonate group and four oxalate ligands, abbreviated as Ox1, Ox2, Ox3 and Ox4. Among these oxalate ligands, the first two are in general positions, while the latter two are inversion symmetric.

A main dense unit, based on Nd atoms and the carbonate group, is localized around the symmetry centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The Nd atoms form a tetranuclear entity that constitutes the main building block of this structure (Fig. 1). One Nd atom, Nd2, and its symmetry equivalent are associated by sharing the O-atom edge O15–O15$^{\rm iv}$, belonging to the carbonate groups [symmetry code: (iv) $1-x, 1-y, 1-z$]. In addition, because of the multidendate coordination of the carbonate group, atom O14 is common to the coordination spheres of both Nd1 and Nd2. The Nd atoms form a parallelogram, with Nd1$\cdots$Nd2 = 4.892 (1) Å and Nd1$\cdots$Nd2$^{\rm iv}$ = 6.427 (1) Å. The shortest Nd$\cdots$Nd distance is between two Nd2 atoms that share the O15–O15$^{\rm iv}$ edge, with Nd2$\cdots$Nd2$^{\rm iv}$ = 4.187 (1) Å.

Starting from the tetranuclear entity, the oxalate ligands are attached to form a rather open structure. The three-dimensional network can be described in the following general way. First, parallel to $[\bar{1}11]$ and [100], Ox3 and Ox4 groups ensure the link between two Nd1 and two Nd2 atoms, respectively, of successive units, *via* atoms O9 and O10, and O11 and O12, respectively. Secondly, in a layer parallel to the (122) plane, Ox1 and Ox2 groups connect the different Nd atoms of neighbouring cells, and all the oxalate ligands build up a distorted ladder arrangement, running parallel to [011] (Fig. 2). The successive –Ox1–Nd–Ox2– sequences constitute the two uprights of this ladder, and Ox3 and Ox4 act alternately as rungs. The ladders are connected by atoms O14. Within a ladder, an approximately square eight-membered $[Nd(C_2O_4)]_4$ ring is encountered. Such rings have been observed many times in mixed ammonium–lanthanide oxalates.

The Nd$\cdots$Nd distances in (I), from both sides of the oxalate groups, fall roughly into two sets, 6.307 (1) and 6.308 (1) Å, and 6.483 (1) and 6.431 (1) Å for Ox1 to Ox4, respectively. The shorter distances are a consequence of the displacement, in the same direction, of the corresponding Nd atoms from the mean plane of Ox1 and Ox2. This eight-membered ring deviates considerably from planarity; the maximum distance of Nd from the mean plane is 1.41 (2) Å. An ellipsoidal void of roughly 0.8 × 3.6 Å (not including the van der Waals radii) is present within this ring. The ammonium ions and the solvate

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water molecule, O*W*2, are localized above and below the centre of this free aperture.

If the structure of (I) is viewed parallel to [$0\bar{1}1$], the network is depicted as smooth sinusoidal ribbons consisting of the sequence –Ox3–(tetrameric unit)–Ox4– (Fig. 3). Such ribbons are practically opposite in phase, leading to channels with an ellipsoidal shape of roughly 2.8 × 10 Å (not including the van der Waals radii). The ammonium ions and the water molecules, solvate (O*W*2) or bound to the Nd atom (O*W*1), are localized in these channels.

Both Nd atoms in (I) exhibit a ninefold coordination, but their coordination schemes differ. They are bound to six oxalate O atoms, belonging to Ox1, Ox2 and Ox3 for Nd1, and Ox1, Ox2 and Ox4 for Nd2. Two carbonate O atoms and one water molecule (O*W*1), or three carbonate O atoms, complete the Nd1 and Nd2 environments, respectively. In both cases, the coordination polyhedron is a distorted monocapped archimedian antiprism. The cap positions correspond to O4$^{\rm ii}$ and O15 for Nd1 and Nd2, respectively [symmetry code: (ii) $1 - x$, $-y$, $1 - z$]. The Nd—O distances are comparable, with a relatively narrow dispersion. The Nd1—O distances range from 2.456 (3) to 2.533 (3) Å, with a mean value of 2.492 Å, the shortest distances being to atom O14 (shared with Nd2) and the ligand water molecule O*W*1 (Table 1). The Nd2—O distances range from 2.435 (3) to 2.542 (3) Å, with the same mean value as for Nd1. Note that the Nd2—O14 and Nd1—O14 distances [2.461 (3) and 2.456 (3) Å, respectively] are similar, and that the Nd1—O14—Nd2 angle of 168.3 (2)° is almost linear.

All the oxalate ligands are bis-chelating. Bond distances and angles for such ligands (Table 1) agree well with the values commonly observed for such complexes. The oxalate groups Ox1 and Ox2, lying on general positions, are almost planar; deviations from the mean planes are smaller than 0.075 (2) and 0.031 (2) Å, respectively.

The carbonate group is bis-chelating to two Nd atoms and monodentate to a third Nd atom. The C—O bond lengths are rather scattered, ranging from 1.247 (5) to 1.310 (5) Å, with a mean value of 1.283 Å, consistent with the values commonly observed (Negro *et al.*, 1977; Palmer & Van Eldik, 1983; Roméro *et al.*, 1997; Trombe *et al.*, 1998). Such a scatter could be a consequence of the carbonate coordination scheme. Atoms O14 and O15 are μ_2-bridging and they correspond to the longest distances, while atom O13 is monodentate and its C—O distance is smaller. The bond-length scatter also seems to affect the bond angles slightly. However, the carbonate group is planar and the three Nd atoms to which it is bound are all at a distance of less than 0.265 (8) Å from the mean plane.

The ammonium ions in (I) have a nearly tetrahedral geometry. As seen for the solvate water molecule, O*W*2, these species exhibit strong hydrogen bonding between themselves,

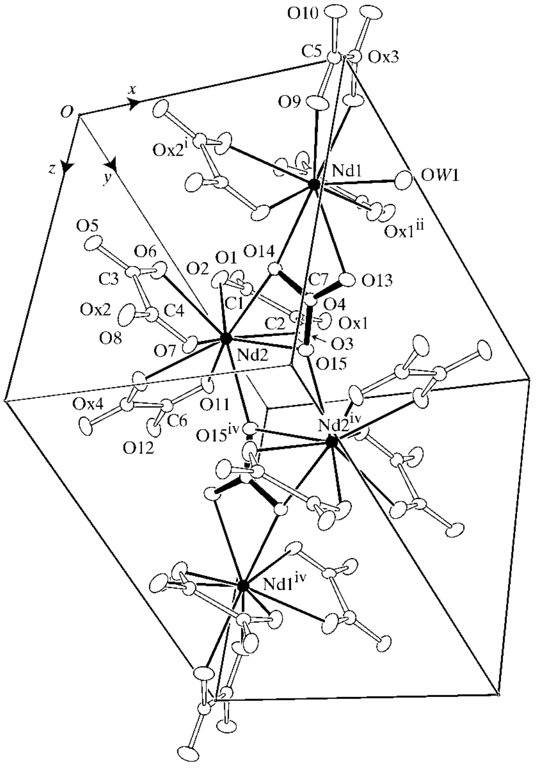

Figure 1
A view of the tetrameric unit formed by the Nd atoms in (I), showing their immediate environment and the carbonate groups. Displacement ellipsoids are drawn at the 50% probability level. For the sake of clarity, the ammonium ions and the solvate water molecule have been omitted. The symmetry codes are as given in Tables 1 and 2.

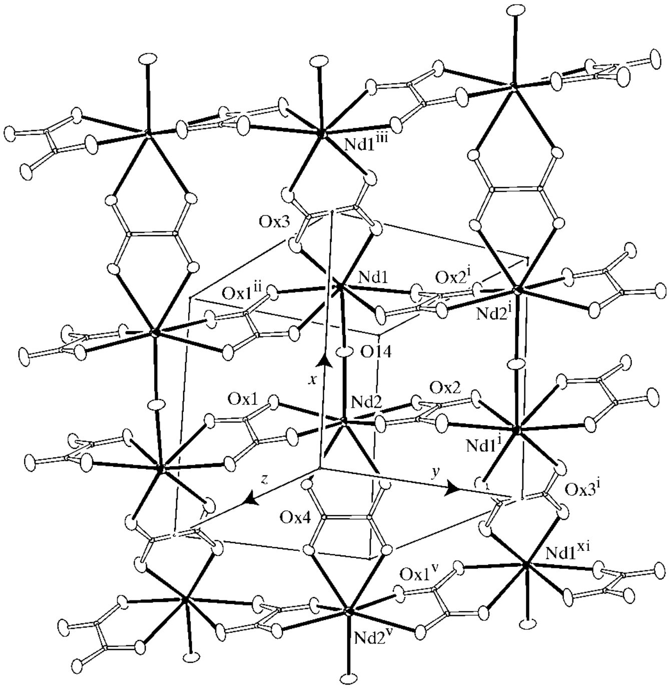

Figure 2
A view of the motif built up by two ladders sharing atoms O14 of the carbonate ions. The water molecules, the ammonium ions and some parts of the carbonate ligand (atoms O13, O15 and C7) have been omitted. The symmetry codes are as given in Tables 1 and 2, plus (xi) $x - 1$, $1 + y$, z.

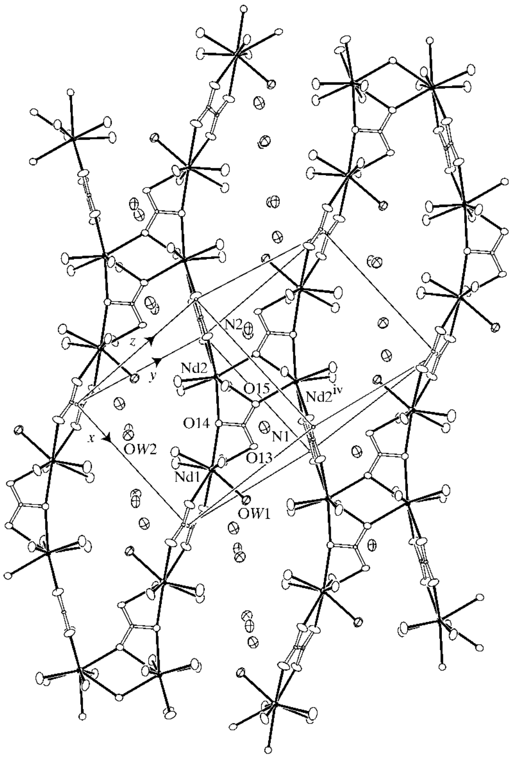

Figure 3
A representation of the –Ox3–(tetrameric unit)–Ox4– sequence that forms the ribbons in the structure of (I). The ammonium ions and the solvate water molecule are intercalated between these ribbons. For clarity, some parts of the oxalate ligands Ox1 and Ox2 (atoms C1, C2, C3 and C4) have been omitted. The symmetry code is as given in Table 1.

the oxalate O atoms of the framework and the ligand water molecule, *O*W1. The *O*W2—H$\cdots$O bonds range from 2.856 (5) to 2.897 (6) Å, while N—H$\cdots$O bonds range between 2.859 (6) and 3.103 (7) Å (Table 2). Note that atoms H7 $(N1H_4)^+$ and H11 $(N2H_4)^+$ are triply and doubly bridging, respectively.

The starting reagents were free of ammonium and carbonate ions. Thus, the formation of these ions must involve the *in situ* decomposition of the guanidinium species under the synthesis conditions. It is well known that this ion is easily hydrolysed in the temperature range 423–473 K, as observed for some amines (imidazole), resulting in ammonium and carbonate species (Chippindale *et al.*, 1996; Trombe *et al.*, 2001).

Experimental

Single crystals of (I) were obtained from neodymium(III) oxalate decahydrate (1 mmol), guanidinium oxalate (2 mmol) and water (10 ml). These reactants were sealed in a Teflon-lined steel bomb (autogeneous pressure) and heated at 423 K for 5 d. After cooling, the resulting product was filtered off, washed with distilled water and dried at room temperature. The theoretical X-ray powder pattern of the single crystal is not representative of the bulk material.

Crystal data

$(NH_4)_2[Nd_2(CO_3)(C_2O_4)_3(H_2O)]\cdot H_2O$
$M_r = 684.67$
Triclinic, $P\overline{1}$
$a = 8.7065\ (10)$ Å
$b = 9.5300\ (10)$ Å
$c = 10.3274\ (10)$ Å
$\alpha = 73.350\ (18)°$
$\beta = 86.90\ (2)°$
$\gamma = 80.50\ (2)°$
$V = 809.69\ (17)$ Å^3
$Z = 2$
$D_x = 2.808$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4700 reflections
$\theta = 2.1$–$29.4°$
$\mu = 6.44$ mm^{-1}
$T = 293\ (2)$ K
Plate, pale purple
$0.22 \times 0.20 \times 0.04$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.239$, $T_{\max} = 0.789$
10 885 measured reflections
4700 independent reflections
4053 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 30°$
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.058$
$S = 0.88$
4700 reflections
302 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0390P)^2 + 2.1271P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.82$ e Å^{-3}
$\Delta\rho_{\min} = -1.80$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0059 (5)

Table 1
Selected geometric parameters (Å, °).

Nd1—O14	2.456 (3)	O2—C1	1.254 (5)
Nd1—*O*W1	2.457 (4)	O3—C2	1.252 (5)
Nd1—O8^{i}	2.469 (3)	O4—C2	1.250 (5)
Nd1—O5^{i}	2.485 (3)	O5—C3	1.256 (5)
Nd1—O1^{ii}	2.493 (3)	O6—C3	1.250 (5)
Nd1—O10^{iii}	2.494 (3)	O7—C4	1.250 (5)
Nd1—O4^{ii}	2.512 (3)	O8—C4	1.255 (5)
Nd1—O13	2.525 (3)	O9—C5	1.242 (5)
Nd1—O9	2.533 (3)	O10—C5	1.251 (5)
Nd2—O15^{iv}	2.435 (3)	O11—C6	1.243 (5)
Nd2—O14	2.461 (3)	O12—C6	1.253 (5)
Nd2—O12^{v}	2.477 (3)	O13—C7	1.247 (5)
Nd2—O2	2.478 (3)	O14—C7	1.310 (5)
Nd2—O7	2.503 (3)	O15—C7	1.293 (5)
Nd2—O6	2.504 (3)	C1—C2	1.551 (6)
Nd2—O11	2.510 (3)	C3—C4	1.554 (6)
Nd2—O15	2.520 (3)	C5—C5^{iii}	1.545 (8)
Nd2—O3	2.542 (3)	C6—C6^{v}	1.550 (8)
O1—C1	1.251 (5)		
O1—C1—O2	126.0 (4)	O8—C4—C3	116.9 (4)
O1—C1—C2	117.7 (4)	O9—C5—O10	126.5 (4)
O2—C1—C2	116.3 (4)	O9—C5—C5^{iii}	117.1 (5)
O4—C2—O3	126.6 (4)	O10—C5—C5^{iii}	116.4 (5)
O4—C2—C1	117.2 (4)	O11—C6—O12	126.1 (4)
O3—C2—C1	116.3 (4)	O11—C6—C6^{v}	117.1 (5)
O6—C3—O5	126.9 (4)	O12—C6—C6^{v}	116.8 (5)
O6—C3—C4	117.0 (4)	O13—C7—O15	124.5 (4)
O5—C3—C4	116.1 (4)	O13—C7—O14	120.0 (4)
O7—C4—O8	125.6 (4)	O15—C7—O14	115.5 (4)
O7—C4—C3	117.5 (4)		

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $1-x, -y, 1-z$; (iii) $2-x, -y, -z$; (iv) $1-x, 1-y, 1-z$; (v) $-x, 1-y, 1-z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O}W1-\mathrm{H1}\cdots\mathrm{O2}^{\mathrm{vi}}$	0.89 (5)	1.81 (5)	2.692 (5)	170 (6)
$\mathrm{O}W1-\mathrm{H2}\cdots\mathrm{O}W2^{\mathrm{vi}}$	0.90 (8)	2.22 (9)	3.018 (6)	148 (6)
$\mathrm{O}W2-\mathrm{H3}\cdots\mathrm{O8}^{\mathrm{vii}}$	0.90 (7)	2.20 (8)	2.897 (6)	134 (7)
$\mathrm{O}W2-\mathrm{H4}\cdots\mathrm{O4}^{\mathrm{ii}}$	0.89 (5)	2.01 (6)	2.856 (5)	159 (7)
$\mathrm{N1}-\mathrm{H5}\cdots\mathrm{O3}$	0.81 (2)	2.23 (2)	3.013 (6)	163 (6)
$\mathrm{N1}-\mathrm{H6}\cdots\mathrm{O1}^{\mathrm{ii}}$	0.82 (4)	2.22 (4)	2.976 (6)	154 (6)
$\mathrm{N1}-\mathrm{H7}\cdots\mathrm{O}W1^{\mathrm{viii}}$	0.83 (4)	2.29 (4)	2.992 (6)	143 (5)
$\mathrm{N1}-\mathrm{H7}\cdots\mathrm{O10}^{\mathrm{ix}}$	0.83 (4)	2.59 (5)	3.067 (6)	118 (5)
$\mathrm{N1}-\mathrm{H7}\cdots\mathrm{O}W2^{\mathrm{ii}}$	0.83 (4)	2.54 (5)	3.103 (7)	126 (5)
$\mathrm{N1}-\mathrm{H8}\cdots\mathrm{O12}^{\mathrm{vi}}$	0.83 (5)	2.07 (4)	2.859 (6)	161 (6)
$\mathrm{N2}-\mathrm{H9}\cdots\mathrm{O7}^{\mathrm{iv}}$	0.81 (3)	2.25 (3)	3.025 (6)	159 (5)
$\mathrm{N2}-\mathrm{H10}\cdots\mathrm{O5}^{\mathrm{ix}}$	0.82 (4)	2.10 (4)	2.891 (6)	162 (5)
$\mathrm{N2}-\mathrm{H11}\cdots\mathrm{O10}^{\mathrm{x}}$	0.83 (4)	2.58 (5)	3.041 (6)	116 (5)
$\mathrm{N2}-\mathrm{H11}\cdots\mathrm{O11}$	0.83 (4)	2.20 (4)	2.927 (6)	146 (5)
$\mathrm{N2}-\mathrm{H12}\cdots\mathrm{O}W2^{\mathrm{ix}}$	0.83 (4)	2.12 (4)	2.930 (6)	166 (6)

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

The H atoms were found in difference Fourier syntheses and refined freely. However, the distances to their parent atoms were idealized with O—H and N—H restraints; the values of the O—H and N—H dimensions are given in Table 2. The assignments of N and O atoms were consistent with the H-atom positions and also with the *U* values.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1509). Services for accessing these data are described at the back of the journal.

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