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Three-Dimensional Open-Framework Neodymium Oxalates with Organic Functional Groups Protruding in 12-Member Channels

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Two open-framework neodymium oxalates, $[NH_3CH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$ (**I**) and $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$ (**II**), have been synthesized hydrothermally in the presence of 1,2-diaminopropane (1,2-DAP) and formic (**I**) and acetic (**II**) acids. The Nd atoms in both these oxalates have 9-fold coordination with respect to the oxygens, with the Nd atom in a distorted monocapped square antiprism coordination in **I** and in an idealized D_{3h} triply capped trigonal prism coordination in **II**. The three-dimensional framework structures of **I** and **II** are built up by *in-plane* linkages between the Nd and the oxalate moieties, forming layers with 12-membered honeycomb-like apertures, pillared by an *out-of-plane* oxalate unit. The 12-memberd channel in **I** contains a dangling formate group in addition to the disordered amine molecule, while in **II**, the channel has *N*-(2-aminopropyl acetimide) molecules formed by the in situ reaction of 1,2-DAP and acetic acid. The accessibility of the formate and *N*-(2-aminopropyl acetimide) functional groups in **I** and **II**, respectively, uniformly distributed within the channels enables chemical manipulation. Crystal data: **I**, monoclinic, space group $P2_1/c$ (no. 14), $M = 459.5$, $a = 9.0279(4)$ Å, $b = 18.1362(8)$ Å, $c = 8.5631(4)$ Å, $\beta = 102.735(10)°$, $V = 1367.56(11)$ Å^3, $Z = 4$, $R_1 = 0.0229$, $wR_2 = 0.0599$ [1782 observed reflections with $I > 2\sigma(I)$]; **II**, triclinic, space group $P\bar{1}$ (no. 2), $M = 454.5$, $a = 8.6222(9)$ Å, $b = 9.5683(10)$ Å, $c = 9.5712(10)$ Å, $\alpha = 109.388(2)°$, $\beta = 98.508(10)°$, $\gamma = 102.361(12)°$, $V = 706.73(13)$ Å^3, $Z = 2$, $R_1 = 0.0446$, $wR_2 = 0.115$ [1730 observed reflections with $I > 2\sigma(I)$].

Introduction

The hydrothermal syntheses of silicates and phosphates with open architectures have been investigated in great detail for their potential applications in industrially important processes.[1,2] During the last couple of years, the family of open-framework solids has been extended to a large number of metal dicarboxylates and other systems.[3−5] Multifunctional ligands have also attracted attention as possible building units of new framework architectures.[6,7] Thus, in a phosphonate−carboxylate of zinc, Stucky and co-workers[8] have established the formation of a new channel structure possessing dangling organic functional groups. Such compounds are expected to exhibit novel molecular recognition properties and chemical reactivity. Synthesis of such structures, however desirable, poses significant challenges due to the high coordination tendency and flexibility of the organic functional groups. On the basis of our experience with the synthesis of open-

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framework oxalates,[9,10] it appeared to us that it may be possible to obtain new oxalates with functionalized channels under suitable synthetic conditions. In this effort, we have been able to isolate two new open-framework oxalates of neodymium, wherein the carboxylate and amino functional groups protrude into 12-member channels. The compounds with the composition $[NH_3CH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$ (**I**) and $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$ (**II**) were synthesized hydrothermally in the presence of 1,2-diaminopropane (1,2-DAP). While the amines in **I** are disordered, they react with the acetic acid forming *N*-(2-aminopropyl acetimide) in **II**. To our knowledge, both these compounds are new and are described here for the first time.

Experimental Section

Synthesis and Initial Characterization. Compounds **I** and **II** were synthesized hydrothermally in the presence of 1,2-DAP. Identical starting compositions were employed for both cases, but with formic and acetic acids in **I** and **II**, respectively. Thus, in a typical synthesis, $1.0Nd^{(III)}(NO_3)\cdot 4H_2O$ (0.33 g):6.2DAP (0.43 mL): $6.1H_2C_2O_4\cdot 2H_2O$ (0.63 g):6.2[HCOOH (0.19 mL)(**I**)/CH_3COOH (0.29 mL)(**II**)]:$67.8H_2O$ were taken and heated in a PTFE-lined stainless steel autoclave at 180 °C for 132 h. The initial pH in both cases was close to 5.0. The formic and acetic acids were added into the synthesis mixture for the possible ligation to the Nd ion to give the ninth coordination, commonly observed in many of the earlier reported layered rare-earth oxalates and carboxylates,[11,12] and thereby functionalizing the channels. The final product containing large quantities of rod-shaped crystals was filtered and washed with deionized water. The yield was about 80% in both cases. The optical examination, combined with X-ray powder diffraction, suggests that no other crystalline product was present. The powder XRD pattern of the powdered single crystals indicated that the product was a new material and the pattern was entirely consistent with the structure determined by single-crystal X-ray diffraction. Typical powder X-ray data for **I** are presented in Table 1. A least-squares (LSQ) fit of the powder XRD lines of **I** gave the following cell: $a = 9.0065(9)$ Å, $b = 18.1069(6)$ Å, $c = 8.5461(9)$ Å, $\beta = 102.68(8)°$, which is in close agreement with that determined by single-crystal XRD (Table 2).

Thermogravimetric analysis (TGA) was carried out under a flow of nitrogen (50 mL/min) from room temperature to 700 °C, using a heating rate of 5 °C min^{-1}. TGA studies indicated a two-step mass loss in the regions 400−450 and 475−600 °C with total mass loss corresponding to 48.5% (calcd 51.8%) and 44.3% (calcd 43.7%) respectively for **I** and **II**. The final decomposed product, presumably $Nd(OH)CO_3$ in both cases, was found to be amorphous by powder XRD. The IR spectroscopy studies of **I** and **II** indicated bands at 1434 cm^{-1} attributed to C=O stretching for the bonded oxalate, and the absence of bands in the region 1690−1730 cm^{-1} (O−H vibration of COOH group) is in agreement with the deprotonated carboxyl group.[6a]

Table 1. Powder X-ray Data for **I**, $[H_3NCH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$

h	K	l	$2\theta_{obs}$	$\Delta(2\theta)^a$	d_{calc}	$\Delta(d)^b$	$I_{rel}{}^c$
1	1	0	11.196	0.004	7.905	−0.003	77
0	1	1	11.702	0.017	7.573	−0.011	100
−1	2	1	16.235	0.002	5.46	−0.001	56
1	1	1	16.92	0.009	5.243	−0.003	44
1	3	0	17.868	0.040	4.975	−0.011	50
0	3	1	18.149	0.005	4.889	−0.001	70
1	2	1	18.957	0.021	4.686	−0.005	62
2	0	0	20.066	−0.146	4.393	0.032	64
2	1	0	20.927	0.122	4.27	−0.025	69
1	3	1	21.778	−0.133	4.056	0.025	54
−2	3	1	25.418	−0.034	3.499	0.005	40
−1	3	2	26.029	−0.096	3.411	0.012	41
2	4	0	28.367	0.061	3.153	−0.007	42
−1	4	2	29.421	0.166	3.053	−0.017	56
−3	2	1	31.703	0.048	2.826	−0.004	34
−1	1	3	31.967	0.013	2.801	−0.001	40
2	1	2	33.095	0.016	2.708	−0.001	43
−3	0	2	33.191	−0.110	2.69	0.009	44
1	6	1	33.881	−0.033	2.643	0.003	48
3	3	0	33.968	−0.054	2.635	0.004	59
1	7	0	36.163	−0.035	2.481	0.003	38
−3	3	2	36.637	0.072	2.457	−0.004	35
1	3	3	39.043	0.006	2.307	0.000	28
−3	1	3	39.854	0.034	2.264	−0.002	43
0	0	4	43.327	−0.084	2.084	0.004	35
3	0	2	41.409	0.028	2.182	−0.002	33
−3	6	1	42.737	0.062	2.119	−0.003	43
2	2	3	43.508	0.170	2.088	−0.008	54
1	5	3	43.952	−0.098	2.056	0.004	44
4	1	1	45.139	−0.074	2.005	0.004	44

[a] $2\theta_{obs} - 2\theta_{calcd}$. [b] $d_{obs} - d_{calcd}$. [c] $100 \times I/I_{max}$.

Table 2. Crystal Data and Structure Refinement Parameters for $[NH_3CH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$ (**I**) and $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$ (**II**)

structural parameter	**I**	**II**
chemical formula	$Nd_1O_{11}C_8N_2H_{15}$	$Nd_1O_{10}C_9N_2H_{14}$
formula mass	459.5	454.5
cryst sym	monoclinic	triclinic
space group	$P2(1)/c$ (no. 14)	$P\bar{1}$ (no. 2)
T/K	293(2)	293(2)
a/Å	9.0279(4)	8.6222(9)
b/Å	18.1362(8)	9.5683(10)
c/Å	8.5631(4)	9.5712(10)
α/deg	90.000(1)	109.388(2)
β/deg	102.735(10)	98.508(10)
γ/deg	90.000(1)	102.361(2)
V/Å^3	1367.56(11)	706.73(13)
Z	4	2
λ/Å	0.71073	0.71073
ρ_{calc}/g cm^{-3}	2.080	2.220
μ/mm^{-1}	3.848	3.738
no. of measd/ obsd reflns	5652/1782	3031/1730
refinement method	full-matrix least-squares on $\lvert F^2 \rvert$	full-matrix least-squares on $\lvert F^2 \rvert$
R1, wR2 [$I > 2\sigma(I)$]	0.0229,[a] 0.0599[b]	0.0446,[a] 0.1150[b]

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max\cdot(F_o^2,0) + 2(F_c)^2]/3$, where $a = 0.0267$ and $b = 3.6124$ for **I** and $a = 0.10000$ and $b = 0.0$ for **II**.

Single-Crystal Structure Determination. A suitable colorless rod-shaped single crystal (0.16 × 0.16 × 0.28 mm^3 for **I** and 0.12 × 0.12 × 0.18 mm^3 for **II**) of each compound was selected and mounted at the tip of a glass fiber with cyanoacrylate (superglue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a Siemens SMART-CCD diffractometer equipped

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Table 3. Selected Bond Distances for Compound **I**, $[NH_3CH_2CH(NH_3)CH_3]$ $[Nd(C_2O_4)_2(HCOO)]\cdot H_2O$[a]

moiety	distance (Å)	moiety	distance (Å)
Nd(1)−O(1)	2.462(4)	O(5)−C(2)#2	1.257(6)
Nd(1)−O(3)	2.477(4)	O(6)−C(4)	1.245(6)
Nd(1)−O(4)	2.480(4)	O(7)−C(4)#3	1.249(6)
Nd(1)−O(7)	2.488(4)	O(8)−C(3)	1.246(6)
Nd(1)−O(2)	2.498(4)	O(9)−C(5)	1.243(8)
Nd(1)−O(5)	2.500(4)	O(3)−C(1)#4	1.255(6)
Nd(1)−O(9)	2.511(4)	O(5)−C(2)#4	1.257(6)
Nd(1)−O(8)#1	2.511(4)	O(7)−C(4)#3	1.249(6)
Nd(1)−O(6)	2.531(4)	C(1)−C(2)	1.562(8)
O(1)−C(3)	1.251(6)	C(3)−C(3)#1	1.550(10)
O(2)−C(2)	1.245(6)	C(4)−C(4)#3	1.545(10)
O(4)−C(1)	1.237(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, $-y$, $-z$; #2, x, $-y + {}^1/_2$, $z - {}^1/_2$; #3, $-x$, $-y$, $-z$; #4, x, $-y + {}^1/_2$, $z + {}^1/_2$.

Table 4. Selected Bond Angles for Compound **I**, $[NH_3CH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$[a]

moiety	angle (deg)	moiety	angle (deg)
O(1)−Nd(1)−O(3)	138.98(12)	O(3)−Nd(1)−O(6)	97.41(12)
O(1)−Nd(1)−O(4)	138.42(12)	O(4)−Nd(1)−O(6)	136.03(13)
O(3)−Nd(1)−O(4)	75.57(13)	O(7)−Nd(1)−O(6)	64.71(12)
O(1)−Nd(1)−O(7)	132.25(12)	O(2)−Nd(1)−O(6)	136.40(13)
O(3)−Nd(1)−O(7)	69.91(12)	O(5)−Nd(1)−O(6)	138.99(13)
O(4)−Nd(1)−O(7)	72.33(13)	O(9)−Nd(1)−O(6)	72.52(14)
O(1)−Nd(1)−O(2)	73.39(12)	O(8)#1−Nd(1)−O(6)	67.81(12)
O(3)−Nd(1)−O(2)	126.19(12)	C(3)−O(1)−Nd(1)	116.9(3)
O(4)−Nd(1)−O(2)	65.61(12)	C(2)−O(2)−Nd(1)	119.7(3)
O(7)−Nd(1)−O(2)	125.87(13)	C(1)#2−O(3)−Nd(1)	120.2(3)
O(1)−Nd(1)−O(5)	95.48(12)	C(1)−O(4)−Nd(1)	120.2(3)
O(3)−Nd(1)−O(5)	65.40(12)	C(2)#2−O(5)−Nd(1)	119.9(3)
O(4)−Nd(1)−O(5)	78.05(14)	C(4)−O(6)−Nd(1)	118.3(3)
O(7)−Nd(1)−O(5)	131.01(12)	C(4)#3−O(7)−Nd(1)	119.3(3)
O(2)−Nd(1)−O(5)	71.09(13)	C(3)−O(8)−Nd(1)#1	114.9(3)
O(1)−Nd(1)−O(9)	75.31(13)	C(5)−O(9)−Nd(1)	134.1(4)
O(3)−Nd(1)−O(9)	141.04(13)	O(4)−C(1)−O(3)#4	125.3(5)
O(4)−Nd(1)−O(9)	86.04(14)	O(2)−C(2)−O(5)#4	127.0(5)
O(7)−Nd(1)−O(9)	71.87(14)	O(8)−C(3)−O(1)	126.1(5)
O(2)−Nd(1)−O(9)	72.73(14)	O(6)−C(4)−O(7)#3	125.6(5)
O(5)−Nd(1)−O(9)	143.80(14)	O(9)−C(5)−N(10)	124.4(7)
O(1)−Nd(1)−O(8)#1	65.28(12)	O(4)−C(1)−C(2)	117.6(5)
O(3)−Nd(1)−O(8)#1	74.11(12)	O(3)#4−C(1)−C(2)	117.1(5)
O(4)−Nd(1)−O(8)#1	143.78(13)	O(2)−C(2)−C(1)	116.8(5)
O(7)−Nd(1)−O(8)#1	114.20(13)	O(5)#4−C(2)−C(1)	116.2(5)
O(2)−Nd(1)−O(8)#1	119.90(13)	O(8)−C(3)−C(3)#1	117.5(6)
O(5)−Nd(1)−O(8)#1	71.61(13)	O(1)−C(3)−C(3)#1	116.4(6)
O(9)−Nd(1)−O(8)#1	130.18(14)	O(6)−C(4)−C(4)#3	117.1(6)
O(1)−Nd(1)−O(6)	72.97(12)	O(7)#3−C(4)−C(4)#3	117.4(6)

[a] Symmetry transformations used to generate equivalent atoms:#1, $-x + 1$, $-y$, $-z$; #2, x, $-y + {}^1/_2$, $z - {}^1/_2$; #3, $-x$, $-y$, $-z$; #4, x, $-y + {}^1/_2$, $z + {}^1/_2$.

Table 5. Selected Bond Distances for Compound **II**, $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$[a]

moiety	distance (Å)	moiety	distance (Å)
Nd(1)−O(1)	2.471(6)	O(5)−C(13)#3	1.237(11)
Nd(1)−O(2)	2.461(6)	O(6)−C(11)	1.267(11)
Nd(1)−O(7)	2.470(8)	O(7)−C(50)	1.21(2)
Nd(1)−O(3)	2.484(6)	O(8)−C(14)	1.246(11)
Nd(1)−O(4)	2.496(7)	O(9)−C(12)#4	1.266(11)
Nd(1)−O(8)	2.494(7)	O(2)−C(14)#1	1.261(11)
Nd(1)−O(6)	2.510(7)	O(5)−C(13)#3	1.237(11)
Nd(1)−O(5)	2.521(6)	O(4)−C(11)#2	1.231(11)
Nd(1)−O(9)	2.529(7)	C(12)−C(12)#4	1.55(2)
O(1)−C(12)	1.246(12)	C(14)−C(14)#1	1.54(2)
O(2)−C(14)#1	1.261(11)	C(13)−C(13)#3	1.54(2)
O(3)−C(13)	1.239(11)	C(11)−C(11)#2	1.53(2)
O(4)−C(11)#2	1.231(11)	C(50)−C(51)	1.562(11)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z + 1$; #2, $-x$, $-y + 1$, $-z + 1$; #3, $-x + 1$, $-y + 1$, $-z + 1$; #4, $-x$, $-y$, $-z$.

Table 6. Selected Bond Angles for Compound **II**, $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$[a]

moiety	angle (deg)	moiety	angle (deg)
O(1)−Nd(1)−O(2)	138.3(2)	O(2)−Nd(1)−O(9)	77.4(2)
O(1)−Nd(1)−O(7)	73.5(2)	O(7)−Nd(1)−O(9)	73.8(3)
O(2)−Nd(1)−O(7)	79.2(2)	O(3)−Nd(1)−O(9)	138.6(2)
O(1)−Nd(1)−O(3)	75.7(2)	O(4)−Nd(1)−O(9)	103.3(2)
O(2)−Nd(1)−O(3)	131.4(2)	O(8)−Nd(1)−O(9)	67.6(2)
O(7)−Nd(1)−O(3)	82.7(3)	O(6)−Nd(1)−O(9)	137.8(2)
O(1)−Nd(1)−O(4)	69.4(2)	O(5)−Nd(1)−O(9)	134.8(2)
O(2)−Nd(1)−O(4)	140.3(2)	C(12)−O(1)−Nd(1)	120.9(6)
O(7)−Nd(1)−O(4)	139.8(2)	C(14)#1−O(2)−Nd(1)	119.9(6)
O(3)−Nd(1)−O(4)	73.7(2)	C(13)−O(3)−Nd(1)	121.2(6)
O(1)−Nd(1)−O(8)	112.7(2)	C(11)#2−O(4)−Nd(1)	120.9(6)
O(2)−Nd(1)−O(8)	65.2(2)	C(13)#3−O(5)−Nd(1)	120.3(6)
O(7)−Nd(1)−O(8)	131.7(2)	C(11)−O(6)−Nd(1)	120.3(6)
O(3)−Nd(1)−O(8)	145.4(2)	C(50)−O(7)−Nd(1)	137.2(9)
O(4)−Nd(1)−O(8)	78.3(2)	C(14)−O(8)−Nd(1)	118.6(6)
O(1)−Nd(1)−O(6)	132.1(2)	C(12)#4−O(9)−Nd(1)	119.5(6)
O(2)−Nd(1)−O(6)	88.1(2)	O(1)−C(12)−O(9)#4	126.0(9)
O(7)−Nd(1)−O(6)	142.3(3)	O(8)−C(14)−O(2)#1	126.5(9)
O(3)−Nd(1)−O(6)	79.4(2)	O(5)#3−C(13)−O(3)	126.2(9)
O(4)−Nd(1)−O(6)	64.5(2)	O(4)#2−C(11)−O(6)	125.8(9)
O(8)−Nd(1)−O(6)	70.4(2)	O(1)−C(12)−C(12)#4	118.3(10)
O(1)−Nd(1)−O(5)	129.8(2)	O(9)#4−C(12)−C(12)#4	115.7(11)
O(2)−Nd(1)−O(5)	67.4(2)	O(8)−C(14)−C(14)#1	117.4(10)
O(7)−Nd(1)−O(5)	72.6(3)	O(2)#1−C(14)−C(14)#1	116.0(10)
O(3)−Nd(1)−O(5)	64.2(2)	O(5)#3−C(13)−C(13)#3	116.6(10)
O(4)−Nd(1)−O(5)	121.9(2)	O(3)−C(13)−C(13)#3	117.2(10)
O(8)−Nd(1)−O(5)	117.4(2)	O(4)#2−C(11)−C(11)#2	118.1(10)
O(6)−Nd(1)−O(5)	69.7(2)	O(6)−C(11)−C(11)#2	116.0(11)
O(1)−Nd(1)−O(9)	65.1(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z + 1$; #2, $-x$, $-y + 1$, $-z + 1$; #3, $-x + 1$, $-y + 1$, $-z + 1$; #4, $-x$, $-y$, $-z$.

with a normal focus, 2.4-kW sealed tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 20 s per frame) in the 2θ range 3−46.6°. Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved by direct methods with SHELXS-86[13] and difference Fourier syntheses. An absorption correction based on symmetry equivalent reflections was applied by using the SADABS program.[14] The amine molecule in **I** as found to be disordered and the formate group was attached directly with the Nd atoms. Similar disorder of the amine molecule, 1,2-DAP, was observed earlier.[15] In the case of **II**, the amine molecule reacted with the acetic acid and was bonded with the Nd center. Due to the disorder of the amine in **I** and reaction in **II**, the hydrogen positions of the amine molecule, though found in the difference Fourier map, were not incorporated in the final refinement. The terminal carbonyl oxygen of the formate group in **I**, found in the difference Fourier map, has a high degree of positional freedom and hence was not included in the refinement. In the case of **II**, the terminal methyl group of the *N*-(2-aminopropyl acetimide) was refined isotropically. The final refinement included atomic positions for all the atoms and anisotropic thermal parameters for all the non-

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(13) Sheldrick, G. M. *SHELXS-86*, A program for the solution of crystal structures; University of Göttingen: Göttingen: Germany, 1986.

(14) Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, Germany, 1986.

(15) Natarajan, S. *J. Solid State Chem.* **1999**, *149*, 50.

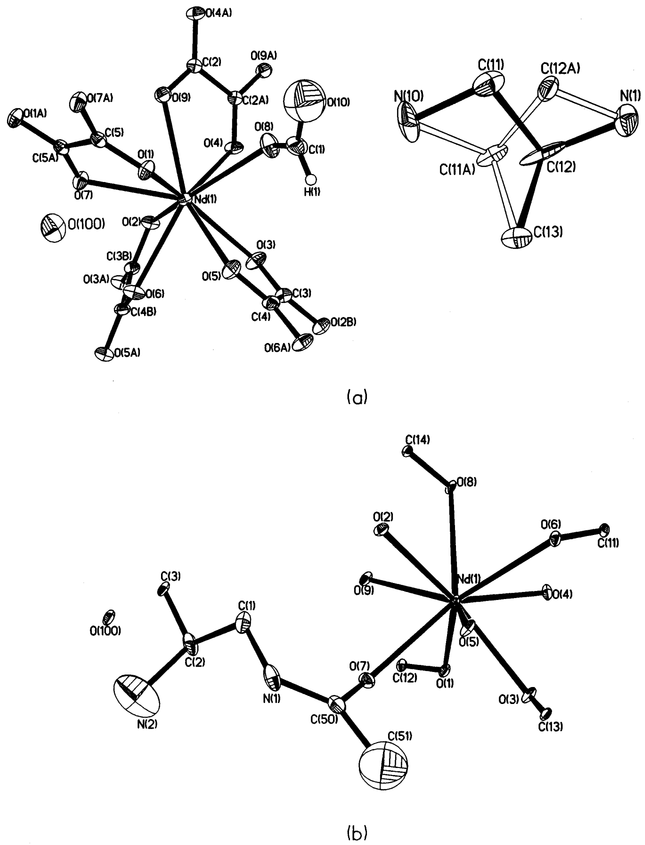


Figure 1. ORTEP diagram for (a) $[NH_3CH_2CH(NH_3)CH_3][Nd(C_2O_4)_2(HCOO)]\cdot H_2O$ (**I**) and (b) $[OC(CH_3)NCH_2CH(CH_3)NH_3][Nd(C_2O_4)_2]\cdot H_2O$ (**II**).

hydrogen atoms other than one oxygen atom in **I** and a carbon atom in **II**. Full-matrix least-squares structure refinement against $|F^2|$ was carried out with the SHELXTL-PLUS[16] package of programs. Details of the final refinements are given in Table 2. The selected bond distances and angles for compounds **I** are presented in Tables 3 and 4 and for **II** in Tables 5 and 6.

Results and Discussion

The asymmetric units of **I** and **II** contains 24 and 23 non-hydrogen atoms (Figure 1a,b). The frameworks of **I** and **II** are built up of linkages between the Nd and the oxalate units, with each Nd atom bound to nine oxygens, which in turn are bound to carbon atoms, forming a network structure. Conversely, the oxalate ions are connected to the neodymium atoms forming the architecture. The Nd atoms have the rare distorted square antiprism coordination capped on one square face (Figure 2a) in **I**. In **II**, the Nd atoms have a common idealized D_{3h} triply capped trigonal prism coordination (Figure 2b).[17] The Nd−O distances are in the range 2.462(4)−2.531(4) Å (av 2.495 Å) for **I** and in the range 2.461(6)−2.529(7) Å (av 2.492 Å) for **II**. The O−Nd−O bond angles for **I** are in the range 65.28(12)−143.80(14)° (av 98.78°) and 64.2(2)−145.4(2)° (av 98.76°) for **II**. The C−O and O−C−O distances and angles are in the expected ranges.

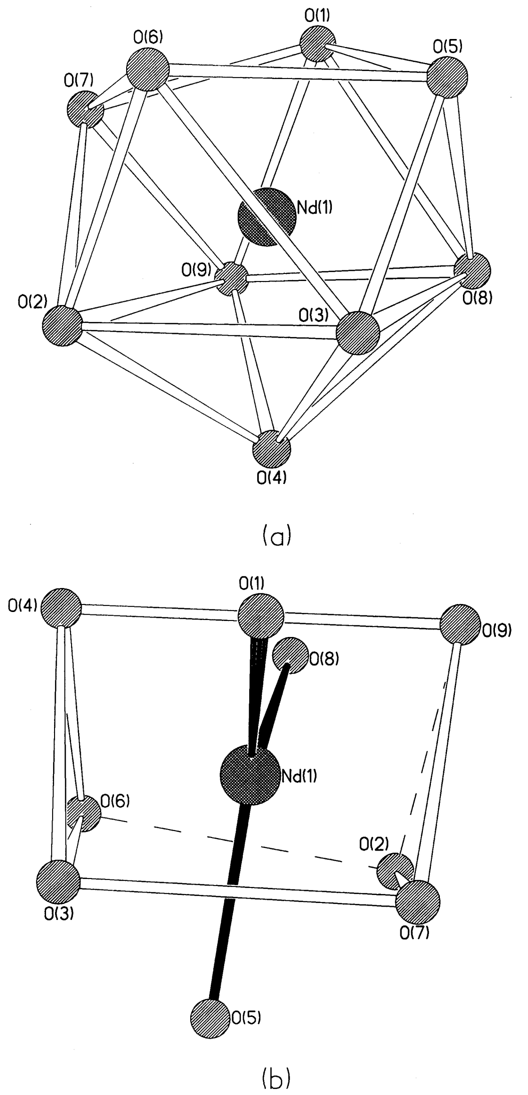
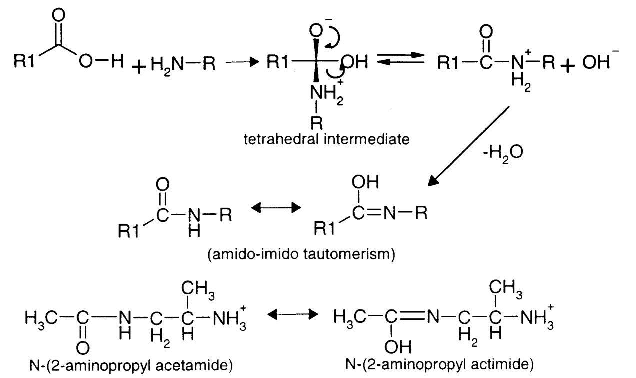


Figure 2. The coordination environment around the Nd atom: (a) the monocapped square antiprism in **I** and (b) the idealized D_{3h} triply capped trigonal prism in **II**.

The organic amine, 1,2-DAP, in **I** is diprotonated and disordered and occupies the center of the 12-membered channels. Such disorder of the amine molecules is observed commonly in open-framework phosphates.[15] The formic acid in the reaction mixture occurs as formate ion in **I** and is coordinated to the Nd atom. Acetic acid in the reaction mixture reacts with 1,2-DAP, in the case of **II**, to form *N*-(2-



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[16] Sheldrick, G. M. *SHELXTL-PLUS*, Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1993.

[17] *Advanced Inorganic Chemistry*, 6th ed.; Cotton, F. A., Wilkinson, G., Murillo, C. A., Bochmann, M., Eds.; John Wiley: New York, 1998.

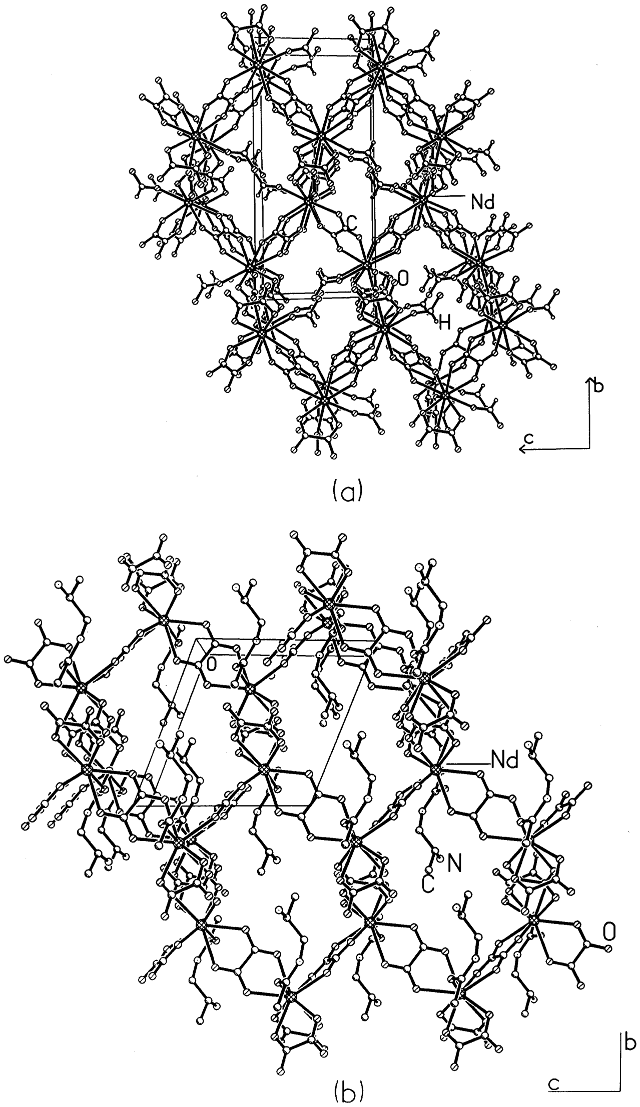

Figure 3. (a) Structure of **I** along the *a* axis showing the 12-membered channels. Note the formate groups protrude into the channel. The amine molecules are not shown for clarity. (b) Structure of **II** along the *a* axis showing the 12-membered channels. Note that the *N*-(2-aminopropyl acetimide) group protrudes into the channel.

aminopropyl acetamide), which occurs in the more stable tautomeric form as *N*-(2-aminopropyl acetimide). A reaction between the acetic acid and the amine occurs through a nucleophilic attack as shown below. The imido compound is linked to Nd through the oxygen atom. The dangling formate in **I** and *N*-(2-aminopropyl acetimide) in **II** both have a high positional freedom.

The framework structures of **I** and **II** can be understood in terms of the simpler building units formed by the linkages between the Nd atoms and the oxalate units. The connectivity between Nd and three oxalate units gives rise to a honeycomb-like layer, with a 12-membered aperture in the *bc* plane. The layers are connected through the fourth oxalate, acting like a pillar, creating the three-dimensional structure with one-dimensional channels as shown in Figure 3a. The ninth coordination of Nd comes from the linkage of one of the oxygen atoms of the formate group in the case of **I**, and from the *N*-(2-aminopropyl acetimide) group in the case of **II** (Figure 3a,b). The connectivity involving the *in-plane* and the *out-of-plane* linkages of the oxalate units, in **I** and **II**, along the *b* and *c* axis gives rise to 12-membered channels, respectively (Figures 4 and 5). Clearly, both **I** and **II** are truly three-dimensional structures with channels along all the crystallographic directions.

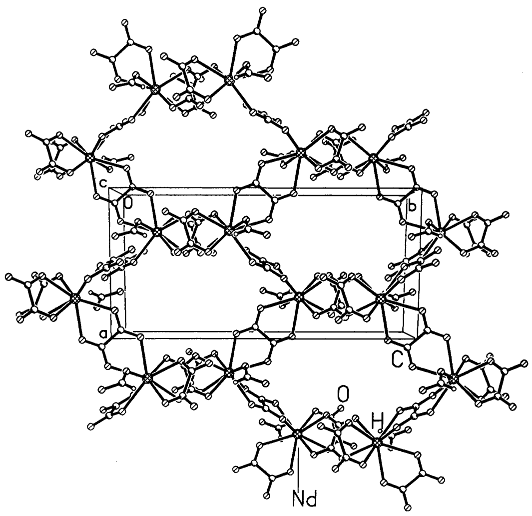

Figure 4. Structure of **I** along the *c* axis showing the 12-membered channel. The disordered amine molecules occupy the center of the channel (not shown).

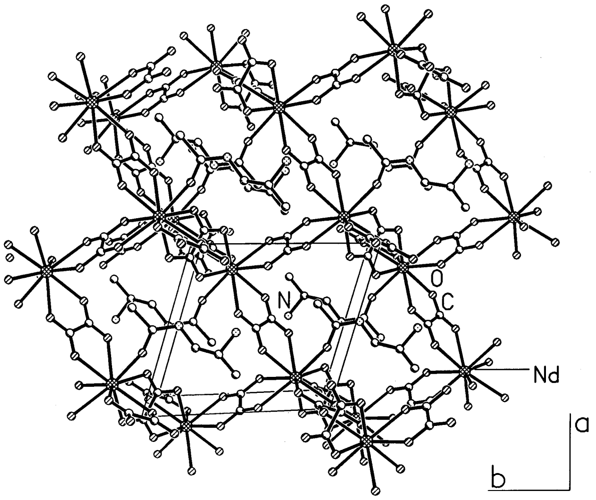

Figure 5. Structure of **II** along the *c* axis showing the 12-membered channel.

The structures of **I** and **II** possess comparable features to those of other framework oxalate structures described recently in the literature.[9,10] Nine coordination for the rare-earth atoms has been encountered in some rare-earth carboxylates earlier, with the ninth coordination being provided by a water molecule.[11,12b] The structures of **I** and **II** are to be contrasted with the Sn(II) and Zn oxalate structures reported recently.[9,10b] In the Sn(II) and Zn oxalates, the Sn and Zn atoms are usually 6-coordinated, resulting in layered architectures for the structures. Although the structure of **II** is comparable to that of an yttrium oxalate reported by us,[10a] the organic species in the latter, 2-methyl-3,4,5,6-tetrahydropyrimid-1-ene, is free and occupies the channels, unlike in **II**, where *N*-(2-aminopropyl acetimide) is directly linked to neodymium. Furthermore, the yttrium atom is eight-coordinated, unlike the bigger Nd, which is nine-coordinated in both **I** and **II**. The higher coordination of the rare-earth atoms in **I**, **II**, and the yttrium oxalate facilitates the formation of three-dimensional structure by having three oxalates coordinated by *in-plane* connectivity and one via *out-of-plane* connection. Such connectivity is reminiscent of the phosphate–oxalate structures, wherein sheets of the inorganic phosphates are cross-linked by the *out-of-plane* oxalate units.[18]

Conclusions

Two new open-framework neodymium oxalates, with dangling organic functional groups uniformly distributed in the channels, are described. These oxalates serve as interesting examples for the effective use of the ninth coordination of the rare-earth ion. The structures differ from those of the yttrium oxalates reported earlier, in that the functional groups are present in the channels of the oxalates described in the present study. The functional groups in **I** and **II** are amenable for chemical manipulation.

Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Mater*. **1999**, *11*, 3216. (b) Choudhury, A.; Natarajan, S.; Rao, C. N. R. *Chem. Eur. J*. **2000**, *6*, 1168.