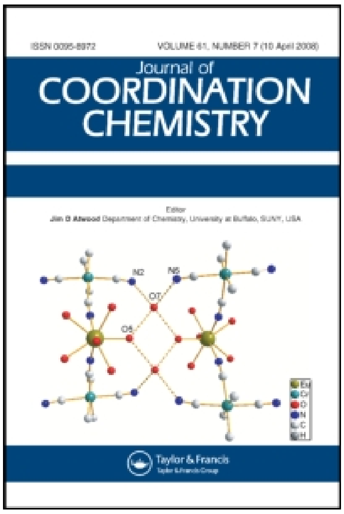

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Syntheses, characterization, and crystal structures of coordination polymers: $\{NH_4 \cdot [Ln(OVA)_4]\}_{<i>n</i>}$ (Ln=Pr, Nd, Gd, and Ho; OVA=2-hydroxy-3-methoxybenzoate)

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Syntheses, characterization, and crystal structures of coordination polymers: $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho; OVA = 2-hydroxy-3-methoxybenzoate)

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The title complexes $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho; OVA = 2-hydroxy-3-methoxybenzoate) were synthesized in water and characterized by FT-IR, elemental analysis, TGA, and X-ray single-crystal diffraction analysis. Two distinct structure types were isolated. Structure type I with formula $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd) contains Ln–COO^- quadruply-bridged helical 1-D chains, with all carboxylates bridging. The structure type II with formula $\{NH_4 \cdot [Ho(OVA)_4]\}_n$ contains bridging and chelating carboxylates, resulting in Ho–COO^- double helical 1-D chains. The passage from type I to type II structure is ascribed to the lanthanide contraction. These 1-D chains are extended to 3-D supramolecular architecture by hydrogen bonds.

Keywords: Coordination polymers; Carboxylate; Crystal structure; Lanthanide complexes

1. Introduction

Metal-organic frameworks (MOFs) have the potential to exhibit useful bulk properties such as nonlinear optical (NLO) behavior [1], novel magnetism [2–4], and guest sorption [5]. Carboxylate networks have received a great deal of attention due to their ability to both chelate a metal and simultaneously bridge to an adjacent metal, especially with large and less rigid coordination spheres of rare earth elements [6–8]. Vanillic(3-methoxy-4-hydroxybenzoic acid, HVA) and *o*-vanillic(2-hydroxy-3-methoxybenzoic acid, HOVA) are widely used in pharmacology, as starting material of some polymer rubbers and a component of polymeric soil organic matter [9]. Both have three functional groups, which are potential coordinating sites to metal ions. Transition metals complexes with vanillic acid were investigated and conditional stability constants were calculated from fluorescence and UV spectra [10]. Copper(II), cobalt(II), and nickel(II) complexes with vanillic acid were synthesized and the crystal structures were determined [11]. The M $\cdots$ M distance is short, associated with the hydrogen bond link

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of the apically coordinated water with the nearest neighbor vanillic hydroxyl group. Structure parameters of uranium(IV) complex indicate that the carboxylic group coordinated uranyl cation is in a bidentate mode in the equatorial plane [12]. Complexes of rare earth metals with HVA were synthesized and their thermal decompositions were investigated by Kula [13]. However, the complexes of rare earth with HOVA have not been reported. In this work, complexes of Pr^{3+}, Nd^{3+}, Gd^{3+}, and Ho^{3+} with HOVA were prepared in water and were characterized by elemental analysis, FT-IR, thermal analysis, and X-ray single-crystal diffraction analysis.

2. Experimental

2.1. *General*

All reagents were of analytical reagent grade and were used without purification. $LnCl_3 \cdot 6H_2O$ (Ln = Pr, Nd, Gd, and Ho) were prepared by dissolving Pr_6O_{11}, Nd_2O_3, Gd_2O_3, and Ho_2O_3 (99.95%) in 1 : 1 concentrated hydrochloric acid. IR data were collected of KBr discs with a Nicolet EQUINX55 FTIR spectrometer in the range 400–4000 cm^{-1}. DSC-TGA analyses were obtained with a Q1000DSC + LNCS + FACS Q600SDT of TA company under flowing air at a heating rate of 10°C min^{-1}. Elemental analysis (C, H, and N) was carried with a German Vario EL III atomic elemental analyzer. The metal contents were determined by titration with xylenol orange indicator following acid digestion and buffering with hexamine [14]. The X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector.

2.2. *Syntheses*

Single crystals of complexes suitable for X-ray analysis were obtained by the method described for $\{NH_4 \cdot [Pr(OVA)_4]\}_n$.

$\{NH_4 \cdot [Pr(OVA)_4]\}_n$: HOVA (0.1008 g, 0.6 mmol) and $PrCl_3 \cdot 6H_2O$ (0.2 mmol, 0.0710 g) were dissolved in 15 mL hot water and the pH of the resulting solution was adjusted to 5 by aqueous ammonia, followed by stirring for 2 h in a water bath (65°C). After several days green needle-like crystals suitable for the X-ray diffraction were filtered and washed first with water three times and then 95% ethanol (yield: 35% based on Pr). Anal. Calcd for $C_{32}H_{32}NO_{16}Pr$: C, 46.43; H, 3.82; N, 1.63; Pr, 16.18. Found: C, 46.40; H, 3.87; N, 1.6; Pr, 17.03%. IR(KBr, cm^{-1}): 3210(m), 1621(m), 1579(s), 1484(m), 1465(m), 1444(m), 1402(vs), 1340(m), 1246(vs), 1060(m), 645(w).

$\{NH_4 \cdot [Nd(OVA)_4]\}_n$: Yield: 30% (based on Nd), Anal. Calcd for $C_{32}H_{32}NO_{16}Nd$: C, 46.30; H, 3.73; N, 1.62; Nd, 17.24. Found: C, 46.22; H, 3.85; N, 1.69; Nd, 17.36%. IR (KBr, cm^{-1}): 3211(w), 1621(m), 1581(vs), 1484(m), 1465(m), 1403(vs), 1348(m), 1340(m), 1247(vs), 1060(m), 646(w).

$\{NH_4 \cdot [Gd(OVA)_4]\}_n$: Yield: 40% (based on Gd), Anal. Calcd for $C_{32}H_{32}NO_{16}Gd$: C, 45.42; H, 3.64; N, 1.64; Gd, 18.31. Found: C, 45.51; H, 3.79; N, 1.66; Gd 18.63%. IR (KBr, cm^{-1}): 3229(m), 1627(w), 1573(vs), 1484(s), 1449(s), 1402(vs), 1347(m), 1246(vs), 1060(m), 485(w).

$\{NH_4 \cdot [Ho(OVA)_4]\}_n$: Yield: 42% (based on Ho), Anal. Calcd for $C_{32}H_{32}NO_{16}Ho$: C, 45.05; H, 3.69; N, 1.47; Ho, 18.52. Found: C, 45.09; H, 3.76; N, 1.64; Ho, 19.37%. IR (KBr, cm^{-1}): 3229(m), 1629(w), 1575(vs), 1489(m), 1454(m), 1411(vs), 1347(m), 1251(vs), 1060(m), 493(w).

2.3. *X-ray crystallography*

Crystals with approximate dimensions were placed on a Bruker Smart APEX CCD area detector. Intensity data were collected using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption. Structures were solved by direct methods using SHELXS-97 [15] and Fourier difference techniques and refined by full matrix least squares on F^2 [16]. All hydrogens were placed in calculated positions. The crystallographic data of the complexes $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho) and the parameters of data collection are summarized in table 1; selected bond lengths and angles are in table 2.

3. Results and discussion

3.1. *Characterization of $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho)*

When complexes formed, the absorption at 1653 cm^{-1} of COOH groups disappears, and asymmetric (ν_{as}) and symmetric (ν_s) vibrations of COO^- appear at 1550–1627 cm^{-1} and 1385–1440 cm^{-1}, respectively. The asymmetric (ν_{as}) and symmetric (ν_s) bands of the COO^- group are split, suggesting that the COO^- groups are bonded in different ways in the same molecule. The absorption bands of phenolic OH and C–O–C in the ligand appear around 1309 and 1240 cm^{-1}, respectively. After formation of complexes, they appear at 1314 and 1247 cm^{-1}, shifted about 5 and 7 cm^{-1}, respectively, indicating that phenolic OH does not coordinate to rare earth ions, in agreement with the X-ray crystal structure. The broad absorption at 3229–3210 cm^{-1} is attributed to $\ddot{o}\S_{N\text{–}H}$ of ammonium cation [17].

The thermal analyses of the complexes were carried out in air with a heating rate of 10°C min^{-1} (figure S1). The complexes are all fairly stable with no weight loss observed to 100°C. The rare earth complexes decompose rapidly over 230°C, with weight loss of 81%; a corresponding exothermic process was observed in the DTG curves. Residual weights of rare earth oxides agree with calculated results.

3.2. *Crystal structure of $\{NH_4 \cdot [Ln(OVA)_4]\}_n$*

Crystal structures of $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho) were determined by X-ray single-crystal diffraction analysis. Complexes $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, and Gd) are allomers and belong to the orthorhombic crystal system, *Pnna* space group, while $\{NH_4 \cdot [Ho(OVA)_4]\}_n$ belongs to the orthorhombic crystal system with space group of *Ccc2*.

Table 1. Crystallographic refinement parameters of $\{NH_4 \cdot [Ln(OVA)_4]\}_n$.

	$(NH_4 \cdot [Pr(OVA)_4])_n$	$(NH_4 \cdot [Nd(OVA)_4])_n$	$(NH_4 \cdot [Gd(OVA)_4])_n$	$(NH_4 \cdot [Ho(OVA)_4])_n$
Empirical formula	$C_{32}H_{32}PrNO_{16}$	$C_{32}H_{32}NdNO_{16}$	$C_{32}H_{32}GdNO_{16}$	$C_{32}H_{32}HoNO_{16}$
Formula weight	827.50	830.83	843.84	851.52
Crystal dimensions (mm^3)	0.40 × 0.26 × 0.07	0.35 × 0.20 × 0.07	0.36 × 0.21 × 0.12	0.41 × 0.16 × 0.12
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (Å, °)	*Pnna*	*Pnna*	*Pnna*	*Ccc2*
a	8.8348(7)	8.8317(1)	8.7945(4)	16.5354(1)
b	16.4800(1)	16.465(2)	16.4014(7)	20.3456(2)
c	22.9332(2)	22.912(3)	22.8534(1)	9.6500(8)
α	90.00	90.00	90.00	90.00
β	90.00	90.00	90.00	90.00
γ	90.00	90.00	90.00	90.00
V (Å^3)	3339.0(5)	3331.7(7)	3296.4(3)	3246.5(5)
Z	6	4	4	4
D_c ($mg\,m^{-3}$)	1.646	1.656	1.700	1.742
Abs. coefficient (mm^{-1})	1.537	1.636	2.090	2.517
F (000)	1672	1676	1692	1704
T (K)	293(2)	293(2)	293(2)	293(2)
Reflections collected	16,706	16,514	16,405	8312
Reflections unique	3075	3064	3035	2887
Observed data [$I > 2\sigma(I)$]	2642	2649	2723	2656
R_{int}	0.0249	0.0237	0.0181	0.0217
Parameters	237	237	237	237
Goodness-of-fit on F^2	0.938	0.977	1.006	1.020
R_1 [$I > 2\sigma(I)$]	0.0206	0.0198	0.0177	0.0192
wR_2	0.0512	0.0521	0.0431	0.0479
Max $\Delta\rho$ (enm^{-3})	257	335	414	809
Min $\Delta\rho$ (enm^{-3})	−523	−708	−468	−610

Table 2. Selected bond lengths (Å) and angles (°) for $\{NH_4\cdot[Ln(OVA)_4]\}_n$.

Panel A: $(NH_4\cdot[Pr(OVA)_4])_n$			
Pr(1)–O(5)#1	2.4088(15)	Pr(1)–O(5)	2.4089(15)
Pr(1)–O(2)#2	2.4322(15)	Pr(1)–O(2)#3	2.4323(15)
Pr(1)–O(1)#1	2.4857(14)	Pr(1)–O(1)	2.4857(14)
Pr(1)–O(6)#2	2.5717(14)	Pr(1)–O(6)#2	2.5717(14)
O(2)–Pr(1)#3	2.4323(15)	O(6)–Pr(1)#3	2.5717(14)
H(1A)–N(1)–H(1B)	110.7(13)	O(5)#1–Pr(1)–O(5)	150.28(8)
O(5)#1–Pr(1)–O(2)#2	77.79(6)	O(5)–Pr(1)–O(2)#2	78.92(6)
O(5)#1–Pr(1)–O(2)#3	78.93(6)	O(5)–Pr(1)–O(2)#3	77.78(6)
O(2)#2–Pr(1)–O(2)#3	76.21(7)	O(5)#1–Pr(1)–O(1)#1	72.88(6)
O(5)–Pr(1)–O(1)#1	135.54(6)	O(2)#2–Pr(1)–O(1)#1	119.17(5)
O(2)#3–Pr(1)–O(1)#1	143.05(6)	O(5)#1–Pr(1)–O(1)	135.54(6)
O(5)–Pr(1)–O(1)	72.88(6)	O(2)#2–Pr(1)–O(1)	143.05(6)
O(2)#3–Pr(1)–O(1)	119.17(5)	O(1)#1–Pr(1)–O(1)	70.31(7)
O(5)#1–Pr(1)–O(6)#2	118.31(5)	O(5)–Pr(1)–O(6)#2	72.70(5)
O(2)#2–Pr(1)–O(6)#2	75.58(5)	O(2)#3–Pr(1)–O(6)#2	142.32(5)
O(1)#1–Pr(1)–O(6)#2	73.68(5)	O(1)–Pr(1)–O(6)#2	73.59(5)
O(5)#1–Pr(1)–O(6)#3	72.70(5)	O(5)–Pr(1)–O(6)#3	118.31(5)
O(2)#2–Pr(1)–O(6)#3	142.32(5)	O(2)#3–Pr(1)–O(6)#3	75.58(5)
O(1)#1–Pr(1)–O(6)#3	73.59(5)	O(1)–Pr(1)–O(6)#3	73.68(5)
O(6)#2–Pr(1)–O(6)#3	139.68(7)		
Panel B: $(NH_4\cdot[Nd(OVA)_4])_n$			
Nd(1)–O(5)#1	2.3963(15)	Nd(1)–O(5)	2.3963(15)
Nd(1)–O(2)#2	2.4700(14)	Nd(1)–O(2)#3	2.4141(14)
Nd(1)–O(1)	2.4700(14)	Nd(1)–O(1)#1	2.4701(14)
Nd(1)–O(6)#2	2.5514(14)	Nd(1)–O(6)#3	2.5514(14)
O(2)–Nd(1)#2	2.4142(14)	O(6)–Nd(1)#2	2.5514(14)
H(1^A)–N(1)–H(1B)	110.2(13)	O(5)#1–Nd(1)–O(5)	150.33(8)
O(5)#1–Nd(1)–O(2)#2	78.96(5)	O(5)–Nd(1)–O(2)#2	77.80(6)
O(5)#1–Nd(1)–O(2)#3	77.80(6)	O(5)–Nd(1)–O(2)#3	78.96(5)
O(2)#2–Nd(1)–O(2)#3	76.24(7)	O(5)#1–Nd(1)–O(1)	135.58(5)
O(5)–Nd(1)–O(1)	72.78(5)	O(2)#2–Nd(1)–O(1)	119.08(5)
O(2)#3–Nd(1)–O(1)	143.03(6)	O(5)#1–Nd(1)–O(1)#1	72.78(5)
O(5)–Nd(1)–O(1)#1	135.58(5)	O(2)#2–Nd(1)–O(1)#1	143.03(6)
O(2)#3–Nd(1)–O(1)#1	119.09(5)	O(1)–Nd(1)–O(1)#1	70.49(7)
O(5)#1–Nd(1)–O(6)#2	72.87(5)	O(5)–Nd(1)–O(6)#2	118.08(5)
O(2)#2–Nd(1)–O(6)#2	75.47(5)	O(2)#3–Nd(1)–O(6)#2	142.38(5)
O(1)–Nd(1)–O(6)#2	73.59(5)	O(1)#1–Nd(1)–O(6)#2	73.78(5)
O(5)#1–Nd(1)–O(6)#3	118.07(5)	O(5)–Nd(1)–O(6)#3	72.87(5)
O(2)#2–Nd(1)–O(6)#3	142.38(5)	O(2)#3–Nd(1)–O(6)#3	75.47(5)
O(1)–Nd(1)–O(6)#3	73.78(5)	O(1)#1–Nd(1)–O(6)#3	73.59(5)
O(6)#2–Nd(1)–O(6)#3	139.76(7)		
Panel C: $(NH_4\cdot[Gd(OVA)_4])_n$			
Gd(1)–O(5)	2.3421(14)	Gd(1)–O(5)#1	2.3421(14)
Gd(1)–O(2)#2	2.3615(14)	Gd(1)–O(2)#3	2.3616(13)
Gd(1)–O(1)	2.4174(13)	Gd(1)–O(1)#1	2.4174(13)
Gd(1)–O(6)#2	2.4929(13)	Gd(1)–O(6)#3	2.4929(13)
O(2)–Gd(1)#3	2.3616(13)	O(6)–Gd(1)#3	2.4929(13)
O(5)–Gd(1)–O(2)#2	78.71(5)	O(5)–Gd(1)–O(5)#1	149.98(8)
O(5)–Gd(1)–O(2)#3	77.80(5)	O(5)#1–Gd(1)–O(2)#2	77.80(5)
O(2)#2–Gd(1)–O(2)#3	76.38(7)	O(5)#1–Gd(1)–O(2)#3	78.71(5)
O(5)#1–Gd(1)–O(1)	135.99(5)	O(5)–Gd(1)–O(1)	72.62(5)
O(2)#3–Gd(1)–O(1)	118.62(5)	O(2)#2–Gd(1)–O(1)	142.89(5)
O(5)#1–Gd(1)–O(1)#1	72.62(5)	O(5)–Gd(1)–O(1)#1	135.99(5)
O(2)#3–Gd(1)–O(1)#1	142.89(5)	O(2)#2–Gd(1)–O(1)#1	118.62(5)
O(5)–Gd(1)–O(6)#2	73.39(5)	O(1)–Gd(1)–O(1)#1	71.40(7)
O(2)#2–Gd(1)–O(6)#2	75.21(5)	O(5)#1–Gd(1)–O(6)#2	117.64(5)

(*continued*)

Table 2. Continued.

O(1)–Gd(1)–O(6)#2	74.38(5)	O(2)#3–Gd(1)–O(6)#2	142.72(5)
O(5)–Gd(1)–O(6)#3	117.64(5)	O(1)#1–Gd(1)–O(6)#2	73.20(5)
O(2)#2–Gd(1)–O(6)#3	142.72(5)	O(5)#1–Gd(1)–O(6)#3	73.38(5)
O(1)–Gd(1)–O(6)#3	73.20(5)	O(2)#3–Gd(1)–O(6)#3	75.21(5)
O(6)#2–Gd(1)–O(6)#3	139.79(6)	O(1)#1–Gd(1)–O(6)#3	74.38(5)
Panel D: $(NH_4\cdot[Ho(OVA)_4])_n$			
Ho(1)–O(6)#1	2.259(3)	Ho(1)–O(6)#2	2.259(3)
Ho(1)–O(5)	2.347(2)	Ho(1)–O(5)#3	2.347(2)
Ho(1)–O(1)	2.399(2)	Ho(1)–O(1)#3	2.399(2)
Ho(1)–O(2)	2.463(3)	Ho(1)–O(2)#3	2.463(3)
Ho(1)–C(1)#3	2.789(3)	O(6)–Ho(1)#4	2.259(3)
O(6)#1–Ho(1)–O(6)#2	91.21(15)	O(6)#1–Ho(1)–O(5)	79.67(9)
O(6)#2–Ho(1)–O(5)	150.05(9)	O(6)#1–Ho(1)–O(5)#3	150.05(9)
O(6)#2–Ho(1)–O(5)#3	79.67(9)	O(5)–Ho(1)–O(5)#3	121.17(11)
O(6)#1–Ho(1)–O(1)	133.48(8)	O(6)#2–Ho(1)–O(1)	84.90(8)
O(5)–Ho(1)–O(1)	81.17(7)	O(5)#3–Ho(1)–O(1)	74.51(7)
O(6)#1–Ho(1)–O(1)#3	84.91(8)	O(6)#2–Ho(1)–O(1)#3	133.48(8)
O(5)–Ho(1)–O(1)#3	74.51(7)	O(5)#3–Ho(1)–O(1)#3	81.17(7)
O(1)–Ho(1)–O(1)#3	129.28(11)	O(6)#1–Ho(1)–O(2)	80.34(9)
O(6)#2–Ho(1)–O(2)	76.08(9)	O(5)–Ho(1)–O(2)	74.30(9)
O(5)#3–Ho(1)–O(2)	123.87(8)	O(1)–Ho(1)–O(2)	53.69(8)
O(1)#3–Ho(1)–O(2)	147.37(8)	O(6)#1–Ho(1)–O(2)#3	76.08(9)
O(6)#2–Ho(1)–O(2)#3	80.35(9)	O(5)–Ho(1)–O(2)#3	123.87(8)
O(5)#3–Ho(1)–O(2)#3	74.30(9)	O(1)–Ho(1)–O(2)#3	147.36(8)
O(1)#3–Ho(1)–O(2)#3	53.69(8)	O(2)–Ho(1)–O(2)#3	146.07(15)
O(6)#1–Ho(1)–C(1)#3	79.44(9)	O(6)#2–Ho(1)–C(1)#3	106.81(9)
O(5)–Ho(1)–C(1)#3	99.52(9)	O(5)#3–Ho(1)–C(1)#3	76.13(8)
O(1)–Ho(1)–C(1)#3	145.72(9)	O(1)#3–Ho(1)–C(1)#3	26.97(8)
O(2)–Ho(1)–C(1)#3	159.63(9)	O(2)#3–Ho(1)–C(1)#3	26.71(9)
O(6)#1–Ho(1)–C(1)	106.81(9)	O(6)#2–Ho(1)–C(1)	79.44(9)
O(5)–Ho(1)–C(1)	76.13(8)	O(5)#3–Ho(1)–C(1)	99.52(9)
O(1)–Ho(1)–C(1)	26.97(9)	O(1)#3–Ho(1)–C(1)	145.72(9)
O(2)–Ho(1)–C(1)	26.71(9)	O(2)#3–Ho(1)–C(1)	159.63(9)
C(1)#3–Ho(1)–C(1)	171.31(15)		

Symmetry transformations used to generate equivalent atoms: $\{NH4\cdot[Pr(OVA)4]\}_n$: #1 $-x+3/2$, $-y$, z; #2 $x+1/2$, y, $-z+1$; #3 $-x+1$, $-y$, $-z+1$. $\{NH_4\cdot[Nd(OVA)_4]\}_n$: #1 $-x+3/2$, $-y$, z; #2 $-x+1$, $-y$, $-z+1$; #3 $x+1/2$, y, $-z+1$. $\{NH_4\cdot[Gd(OVA)_4]\}_n$: #1 $-x+3/2$, $-y$, z; #2 $x+1/2$, y, $-z+1$; #3 $-x+1$, $-y$, $-z+1$. $\{NH_4\cdot[Ho(OVA)_4]\}_n$: #1 $-x+2$, y, $z-1/2$; #2 x, $-y$, $z-1/2$; #3 $-x+2$, $-y$, z; #4 x, $-y$, $z+1/2$.

Crystal structures of $\{NH_4\cdot[Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, and Gd), figure 1, show the molecular structure and coordination environment of $\{NH_4\cdot[Gd(OVA)_4]\}_n$. The Gd(III) is coordinated by eight oxygens from eight different carboxyl groups. The coordination geometry around Gd(III) can be described as a distorted square antiprismatic configuration (figure S2). For each Gd(III), four oxygens (O1, O5, O2A, and O6A) of four bridging carboxyl groups form a square face of the square anti-prism. Another square face is formed by another four oxygens (O1A, O5A, O2B, and O6B). The torsion angle O1–O5–O2A–O6A and O1A–O5A–O2B–O6B are both 1.11°, and the deviations of the O atoms from their least-squares plane are negligible.

There are two kinds of O–C–O bond angles in the Gd complex (O2–C1–O1 = 123.0°, O6–C9–O5 = 125.0°). The average bond angle of O–C–O in the Gd complex is 124.0°, smaller than that of the trifluoroacetate and trichloroacetate lanthanide complexes (128.9°) [18, 19]. All carboxylates in complexes bridge rare earth ion and 1-D

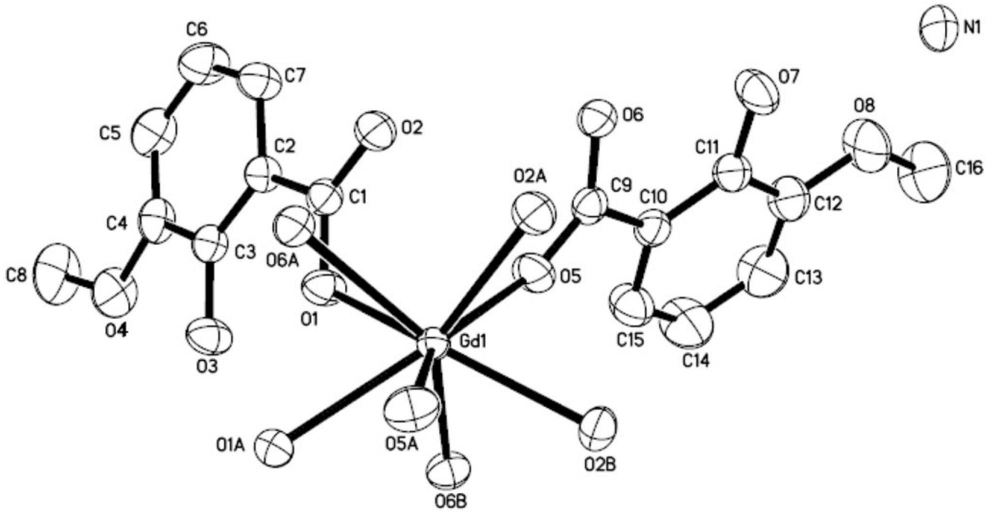

Figure 1. Molecular structure of $\{NH_4 \cdot [Gd(OVA)_4]\}_n$.

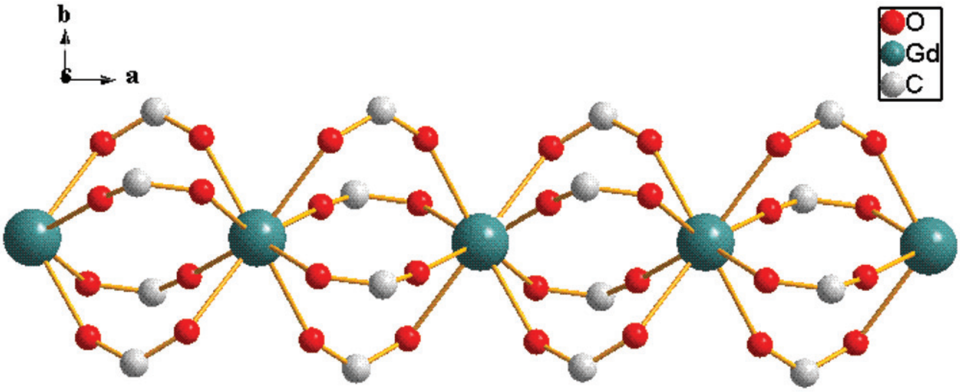

Figure 2. Gd–COO$^-$ helical 1-D chain along the *a* axis of $\{NH_4 \cdot [Gd(OVA)_4]\}_n$.

carboxylate-bridged metal chains are formed, which may be viewed as a Ln–COO$^-$ helix (figure 2). The Gd(III) ions are laid in a zigzag way along the *a* axis. The angle of Gd–Gd–Gd in the complex is 156.57° and the distance of Gd···Gd in the complex is 4.491 Å, too far for a metal-metal bond.

In this supramolecular polymer, each –OH forms an intramolecular hydrogen bond with adjacent –OCH_3, and each hydrogen of NH_4^+ forms two intermolecular hydrogen bonds with two adjacent chains (table 3), resulting in formation of 3-D networks in the complex (figure S3). The hydrogen bonds play a critical role in forming the 3-D networks.

The structure of $\{NH_4 \cdot [Pr(OVA)_4]\}_n$ and $\{NH_4 \cdot [Nd(OVA)_4]\}_n$ are the same as $\{NH_4 \cdot [Gd(OVA)_4]\}_n$. The Pr···Pr (4.516 Å) and Nd···Nd (4.513 Å) distances are both longer than that of Gd···Gd (4.491 Å). The average angle of carboxylate in the Pr and Nd complexes are 123.63° and 123.64°, respectively, both smaller than the

Table 3. Hydrogen bond lengths (Å) and angles (°) for $\{NH_4 \cdot [Ln(OVA)_4]\}_n$.

D–H···A	D–H (Å)	H···A (Å)	D–A (Å)	∠D–H···A (°)
$(NH_4 \cdot [Pr(OVA)_4])_n$				
O(3)–H(3)···O(1)	0.82	1.77	2.496(2)	146.5
O(7)–H(7)···O(6)	0.82	1.82	2.545(2)	146.9
N(1)–H(1B)···O(7)	0.938(9)	2.065(17)	2.8677(19)	142.7
N(1)–H(1A)···O(3)	0.940(9)	1.960(13)	2.869(2)	162.0
$(NH_4 \cdot [Nd(OVA)_4])_n$				
O(3)–H(3)···O(1)	0.82	1.77	2.4946(6)	147.2
O(7)–H(7)···O(6)	0.82	1.82	2.5485(5)	147.5
N(1)–H(1A)···O(3)	0.94	1.97	2.8745(6)	161.6
N(1)–H(1A)···O(4)	0.94	2.40	3.0474(6)	126.7
N(1)–H(1B)···O(7)	0.94	2.07	2.8672(5)	141.1
N(1)–H(1B)···O(8)	0.94	2.51	3.2097(1)	131.6
$(NH_4 \cdot [Gd(OVA)_4])_n$				
O(3)–H(3)···O(1)	0.82	1.78	2.5039(2)	146.2
O(7)–H(7)···O(6)	0.82	1.83	2.5530(3)	147.3
N(1)–H(1A)···O(3)	0.94	1.99	2.8909(2)	160.4
N(1)–H(1A)···O(4)	0.94	2.35	3.0118(4)	127.1
N(1)–H(1B)···O(7)	0.94	2.07	2.8665(5)	141.2
N(1)–H(1B)···O(8)	0.94	2.48	3.1697(2)	130.6
$(NH_4\ [Ho(OVA)_4])_n$				
O(3)–H(3)···O(1)	0.82	1.83	2.5435(3)	145.3
O(7)–H(7)···O(5)	0.82	1.85	2.5677(2)	145.2
N(1)–H(1A)···O(7)	0.85	2.20	2.9814(2)	152.2
N(1)–H(1A)···O(8)	0.85	2.36	2.8888(4)	121.1
N(1)–H(1B)···O(3)	0.85	2.16	2.9683(5)	158.2
N(1)–H(1B)···O(4)	0.85	2.48	3.0296(2)	123.3

Gd complex. The lanthanide contraction causes the Ln–O bond length, Ln···Ln distance (table 2), and the cell parameters *a*, *b*, *c* (table 1) to decrease with the increase in atomic number. Lanthanide contraction was also invoked by Li and co-workers to explain analogous results observed in a series of compounds of rare earth metals with 3,5-pyrazoledicarboxylate [20–22].

In contrast to Pr, Nd, and Gd complexes, $\{NH_4 \cdot [Ho(OVA)_4]\}_n$ is *Ccc2* space group and has entirely different coordination environment. The asymmetric unit of Ho complex consists of a Ho(III) ion and four OVA ligands. Each Ho(III) is surrounded by eight oxygens, four (O5, O6, O5A, O6A) from four bridging carboxylates and the other four (O1, O2, O1A, O2A) from two chelating carboxylates, giving a slightly distorted square anti-prismatic geometry (figure 3).

The average Ho–O bond length is 2.367 Å, shorter than that of the Pr, Nd, and Gd complexes, and consistent with the lanthanide contraction. Each Ho(III) is bridged by two carboxylates, forming a $Ln–COO^-$ double helix (figure 4). The dihedral angle between the benzene ring of the two bridging ligands is 5.593°, nearly parallel. The dihedral angle between the benzene rings of the two chelating ligands is 51.051°. The Ho–Ho–Ho angle is 180°, different from that of the Pr, Nd, and Gd complexes (table 2). The Ho···Ho distance is 4.825 Å, longest of the four complexes, attributed to only two bridging carboxylates between two Ho(III) ions. The carboxylate-bridged 1-D double helical chains are connected through hydrogen bonds to form a 3-D supramolecular network (figure S4).

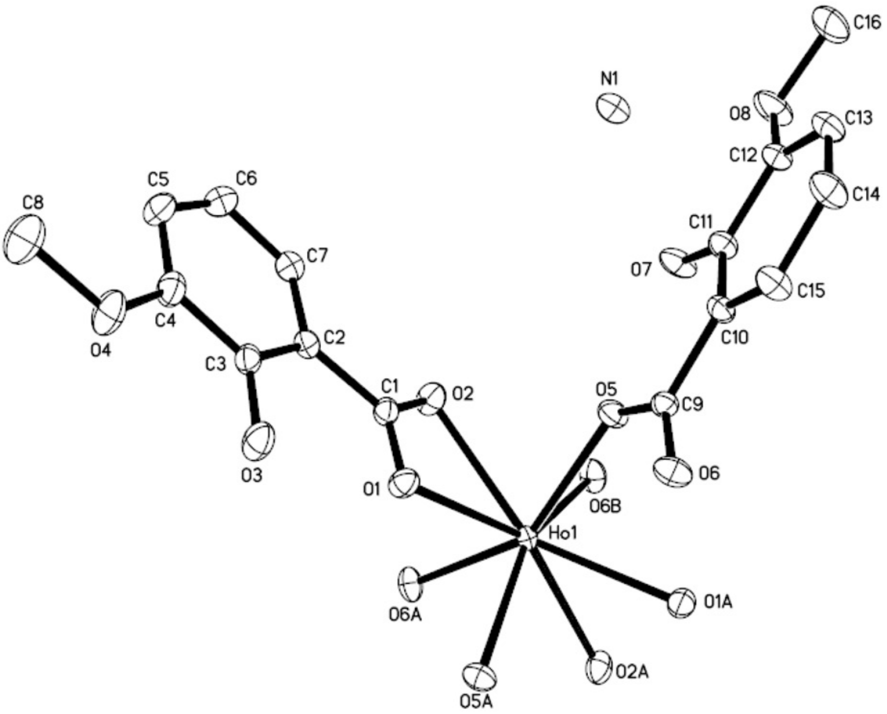

Figure 3. Molecular structure of $\{NH_4 \cdot [Ho(OVA)_4]\}_n$.

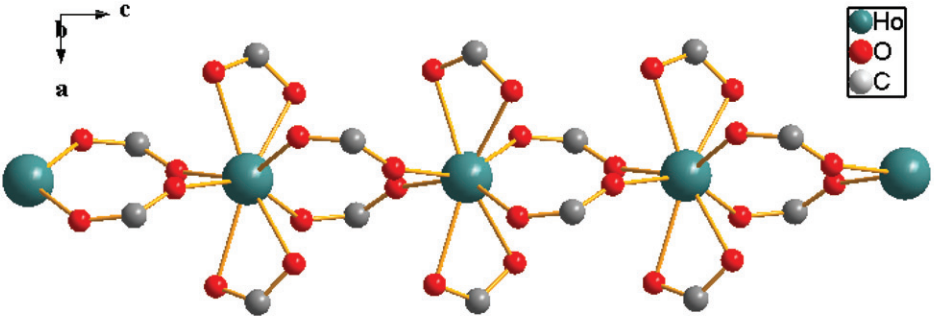

Figure 4. Ho–COO$^-$ double helical 1-D chain along the *c* axis of $\{NH_4 \cdot [Gd(OVA)_4]\}_n$.

4. Conclusion

We report the syntheses and crystal structures of 3-D supramolecular polymers, $\{NH_4 \cdot [Ln(OVA)_4]\}_n$ (Ln = Pr, Nd, Gd, and Ho; OVA = 2-hydroxy-3-methoxybenzoate). The rare earth ions are all eight-coordinate with similar synthesis, but two distinct structure types. When the Ln(III) ion changes from Pr(III) to Gd(III), the structures of the complexes are very similar with carboxylates bridging, forming Ln–COO$^-$ quadruply-bridged helical 1-D chains. Comparing Ho with Pr, Nd, and Gd, the radius of Ho is smaller, causing changes in the coordination of carboxylate, resulting in

Ho–COO$^-$ double helix 1-D chains. The lanthanide contraction plays an important effect in the structures of these complexes.

Supplementary information

Full crystallographic data have been deposited with the CCDC (666140, 666415, 665193, and 665194). These data may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223336 033 or Email: deposit@ccdc.cam.ac.uk).

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