# Synthesis and Characterization of a Series of Lanthanide Complexes Constructed from Orotic Acid

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The solution reaction of orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, $H_3dtpc$) and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = La, Ce) or $Ln_2O_3$ (Ln = Pr, Nd) yielded five complexes $[\{Ln(^aH_2dtpc)_2(^bH_2dtpc)(H_2O)_4\} \cdot H_2O]_n$ (Ln = La **1**, Ce **3**), $[La(^aH_2dtpc)_2(^cH_2dtpc)(H_2O)_6] \cdot 4H_2O$ (**2**), and $[Ln(^aH_2dtpc)_2(OH)(H_2O)_6] \cdot (H_3dtpc)_2 \cdot 7H_2O$ (Ln = Pr **4**, Nd **5**). Complexes **1** and **3** possess 1D chain structures, **2** is a mononuclear structure, and **4** and **5** are mononuclear complexes that are extended into infinite honeycomb structures through hydrogen bonding interactions. The hydrothermal reaction of orotic acid and $Ln_2O_3$ (Ln = La, Nd, Eu, Gd, Er) produced five polymeric complexes $[Ln(^dHdtpc)(OH)(H_2O)]_n$ (Ln = La **6**, Nd **7**, Eu **8**, Gd **9**, Er **10**), which contain isostructural 3D frameworks with ladder-like chains formed by $Ln^{III}$, a $\mu_3$-OH bridge and an orotate spacer.

## Introduction

Lanthanide complexes are of great interest because of their various potential applications in magnetic materials, Ln-doped semiconductor technology, nonlinear optical devices, catalysts, molecular sensors and probes.[1−6] Due to the unique nature of lanthanide ions, such as their large radius, high coordination number and the existence of many single electrons the assembly of lanthanide complexes possessing novel structures and special properties offers great challenges and opportunities in terms of controlling their shapes and dimensions. The selection of an appropriate organic ligand along with different synthetic methods is a key step for the construction of lanthanide complexes with the desired features. It has been proved that ligands containing a combination of nitrogen and oxygen donor atoms are good building blocks for the formation of lanthanide coordination polymers;[7,8] orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, $H_3dtpc$) may therefore be a good ligand for the construction of lanthanide complexes. Aside from its significance in biological systems,[9] orotic acid possesses a fascinating coordination behavior with potential hydrogen-bonding interactions, such as asymmetric geometry and multiple coordination sites.[10] However, previous studies on the coordination chemistry of orotic acid mainly focused on transition metals[11−19] or alkali metals;[20−22] the lanthanides have been neglected. Recently we began to use orotic acid as an organic ligand for the synthesis of lanthanide complexes with the aim of studying the coordination chemistry of the lanthanide-orotic acid system and to obtain some novel structures. We have successfully synthesized two novel lanthanide polymers containing orotic acid by employing a hydrothermal technique.[23,24] This paper reports systematic studies on the synthesis and characterization of a series of lanthanide-orotic acid complexes. We will show that the structures of lanthanide-orotic acid complexes are influenced by the synthetic methods, the lanthanide contraction and the pH.

## Results and Discussion

### Preparation of the Complexes

The coordination chemistry of $H_3dtpc$ with transition metals has been studied in detail in recent years,[11−19] although systematic studies on lanthanide systems have received scant attention. Our aim was to investigate the coordination chemistry of Ln-orotate (Ln is a lanthanide metal) and hoped to obtain novel structures with special properties as well as to study the effects of the lanthanide contraction and acidity on the structure formation. Ten complexes with four kinds of structures were successfully isolated by employing different synthetic techniques.

The solution reactions of lanthanide nitrate or oxide and orotic acid generated the lanthanum complexes **1** and **2** (pH 4−5), the cerium complex **3** (pH 4−5), the praseodymium complex **4** (pH 3−4), and the neodymium complex **5** (pH 3−4). The successful isolation of **1**−**5** prompted us to ex-

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tend our work to other metals of the lanthanide series. However, when we carried out similar reactions of $Ln(NO_3)_3 \cdot nH_2O$ or $Ln_2O_3$ (Ln = Sm−Lu) and orotic acid in water, only uncharacterized precipitates were obtained, which may be due to the effects of the lanthanide contraction. The lanthanide contraction from La to Lu results in a gradual decrease of the ionic radius and of the pH value of the incipient precipitate with increasing atomic number.[25] We therefore tried to lower the pH value to 2 or 1 by addition of dilute HCl or $HNO_3$, but only single crystasl of orotic acid itself were isolated,[26] probably because orotic acid is not deprotonated at such low pH values and therefore cannot coordinate to lanthanide ions.

In order to investigate the effects of the lanthanide contraction and acidity on structure formation, similar experiments were carried out under hydrothermal conditions. The hydrothermal reaction of $Ln_2O_3$ (Ln = La, Nd, Ea, Gd, Er) and orotic acid (1:2) in aqueous solution (pH 7) yielded complexes **6−10**, which are all unexpectedly isomorphous. Taking account of the deprotonation process

$$H_3dtpc \rightleftarrows H_2dtpc^- + H^+ \rightleftarrows Hdtpc^{2-} + 2\,H^+ \rightleftarrows dtpc^{3-} + 3\,H^+$$

we tried to lower pH values of the reaction systems, hoping to obtain different structures. However, similar results were obtained although the yields or purity of the products were different. This result illustrates that complexes **6−10** are the most stable form under hydrothermal condition and their structures are not affected by the pH values of the reaction systems and lanthanide contraction, in contrast to previous observations.[8a,27]

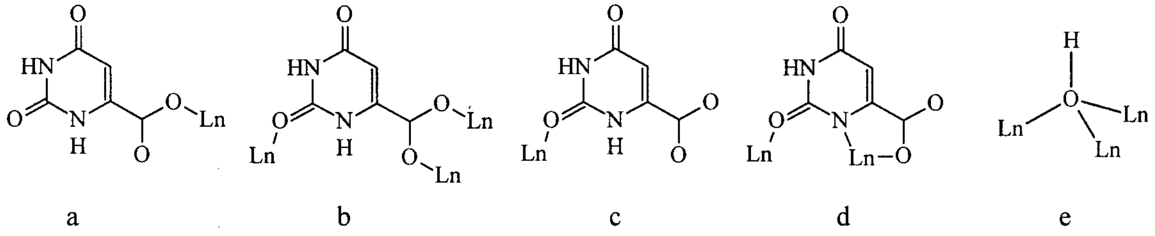
It is interesting that the pH and the lanthanide contraction do, however, have an effect on the structures observed from the solution reactions: the La and Ce complexes were isolated at pH 4−5 and the Pr and Nd complexes were isolated at pH 3−4; no complexes suitable for X-ray analyses were successfully isolated from the solution reactions for the lanthanide elements heavier than neodymium. The different results between the solution and hydrothermal reactions may be caused by different reaction mechanisms:[28] the hydrothermal reaction mechanism is shifted from the thermodynamic to the kinetic domain when compared to a high-temperature solid-state reaction or from the kinetic to the thermodynamic domain when compared to a conventional solution reaction. Thus, the compounds obtained from hydrothermal reactions are often different to those obtained from conventional solution reactions.

## Crystal Structures

X-ray diffraction studies revealed that complexes **1** and **3** are allomers with one-dimensional chain structures. Two types of coordination modes of orotate ligands are present in the structures: one adopts a monodentate fashion to coordinate one $Ln^{III}$ ion through its carboxylate group ($^aH_2dtpc^-$, a in Scheme 1), and the other one acts as a $\mu_3$-bridge to link three $Ln^{III}$ atoms, in which a deprotonated carboxylic group bridges two $Ln^{III}$ ions and the carbonyl oxygen atom connects to another $Ln^{III}$ ion ($^bH_2dtpc^-$, b in Scheme 1). The central La or Ce is coordinated by four carboxylate oxygens and one carbonyl oxygen from different orotate ligands, and four oxygen atoms from coordinated water molecules (see **a** in Figure 1), with the Ln−O distances ranging from 2.497(4) to 2.626(4) Å and from 2.484(2) to 2.598(3) Å for **1** and **3**, respectively. Two $Ln^{3+}$ ions are linked by two bridging carboxylate groups of $^bH_2dtpc^-$ to form a binuclear unit $[Ln_2(^aH_2dtpc)_4(^bH_2dtpc)_2(H_2O)_8]$, which can be viewed as the basic building block for the two complexes. Every two such blocks are connected by $Ln{-}O_{carbonyl}$ bonding to yield a 1D chain (Figure 2). The chains are further joined by different kinds of hydrogen bonding to generate the final 3D framework (Figure 3).

Complex **2** has a mononuclear structure (see **b** in Figure 1) in which the orotate ligands have two types of modes: one binds in a monodentate fashion to coordinate one $Ln^{III}$ ion through its carboxylate group ($^aH_2dtpc^-$, **a** in Scheme 1), and the other one coordinates to a $Ln^{III}$ ion through its carbonyl oxygen atom ($^cH_2dtpc^-$, **c** in Scheme 1). It should be noted that the carboxylate oxygen atoms in $^cH_2dtpc^-$ remain free and do not coordinate to metal ions; this is the first observation of such an interesting coordination mode for the orotate ligand. The $La^{III}$ atom is nine-coordinate, with bonds to two carboxylate and one carbonyl oxygen atoms of different orotate ligands, and six coordinated water oxygen atoms, with La−O distances ranging from 2.486(4) to 2.610(4) Å. The hydrogen bonding provided by the isolated water molecules in the crystal lattice extends complex **2** into a 3D structure (Figure 4).

Complex **4** is also mononuclear, and each local coordination unit around the metal ion contains four orotate ligands (see **c** in Figure 1), two of which are not engaged in coordination to the metal ion as they are not deprotonated; the other two coordinate to the $Pr^{III}$ ion through the deprotonated carboxylic oxygen atoms ($^aH_2dtpc^-$, **a** in



Scheme 1

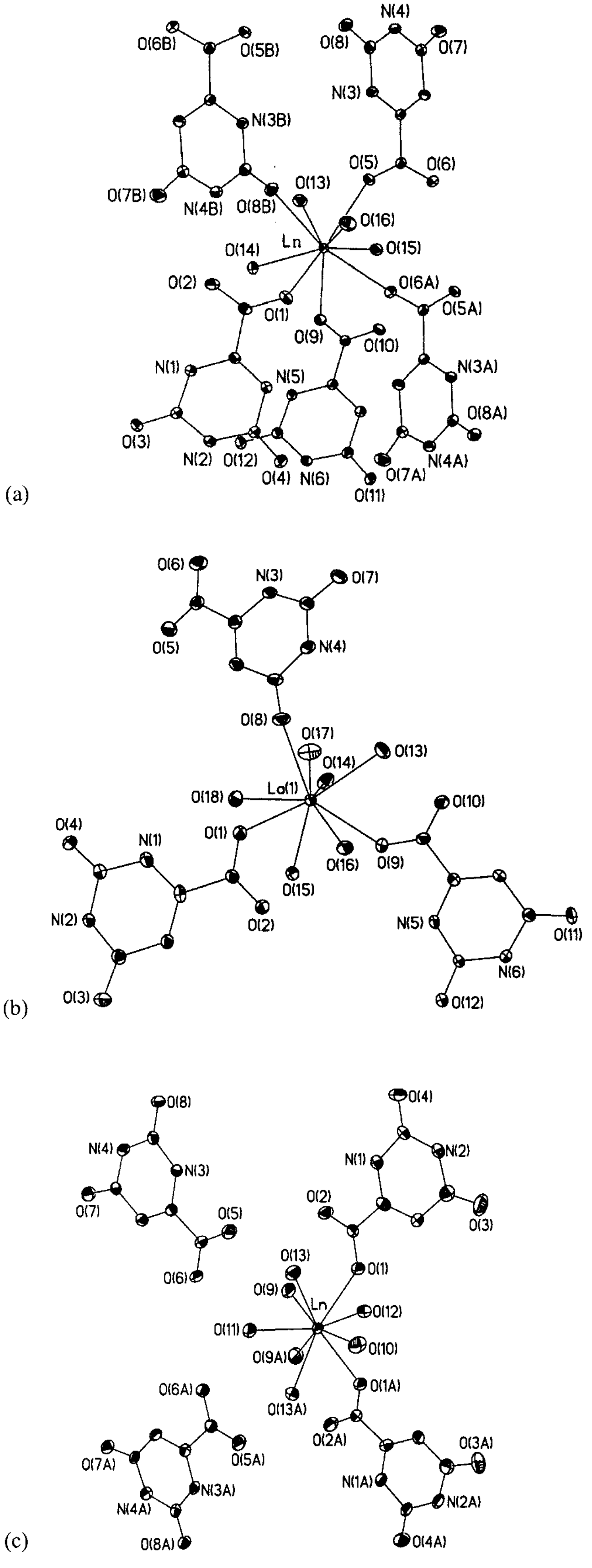


Figure 1. Local coordination environment of metal ions: (a) for **1** and **3**; (b) for **2**; (c) for **4** and **5**

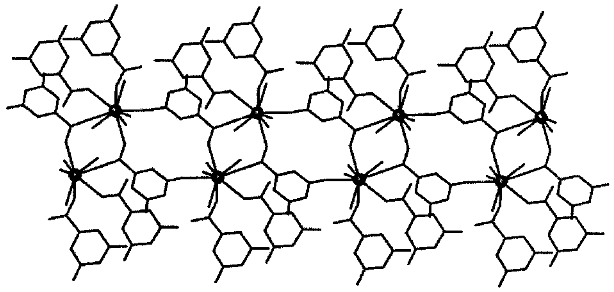


Figure 2. The 1D chain structure for **1** and **3**

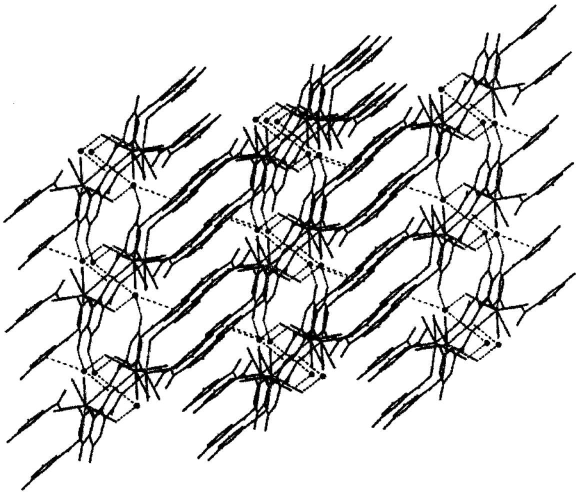


Figure 3. Packing structure along the *b* axis of **1** and **3**

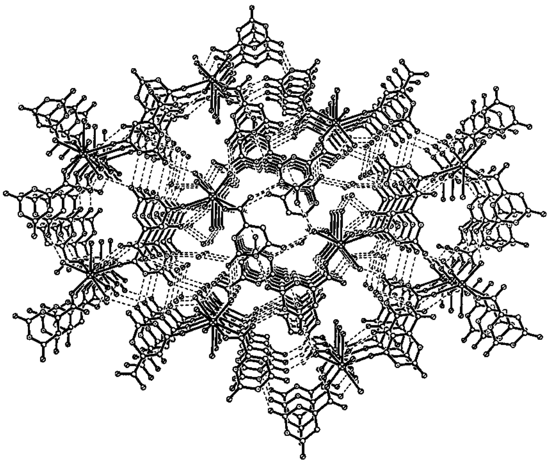


Figure 4. Packing structure along the *a* axis of **2**

Scheme 1). The $Pr^{III}$ ion is nine-coordinate, with bonds to two carboxylate oxygen atoms from different orotate ligands, one oxygen atom from a hydroxyl group and six oxygen atoms from coordinated water molecules, with Pr−O distances ranging from 2.473(6) to 2.620(6) Å. Two coordinated units form a pore-like structure through hydrogen-bonding interactions between orotate ligands and metal ions; such pore-like units are further extended into 2D framework in the *ab* plane. The uncoordinated orotate ligands are located between two neighboring 2D layers, and strong π-π stacking interactions between the heterocyclic rings of uncoordinated and coordinated orotate ligands are observed, with distances from 3.20 to 3.60 Å.

The presence of this intermolecular hydrogen bonding and the π-π stacking interaction finally results in a honeycomb-like 3D structure along the *c* axis with unique quasi-channels (see **a** in Figure 5) accommodating a great number of guest water molecules; the free orotate and coordinated orotate ligands are arranged alternately in the 3D framework (see **b** in Figure 5). Because the hydrogen atoms on the isolated water and coordinated water molecules cannot be assigned completely from the Fourier peaks, the potential hydrogen bonding for complexes **4** and **5** is not discussed.

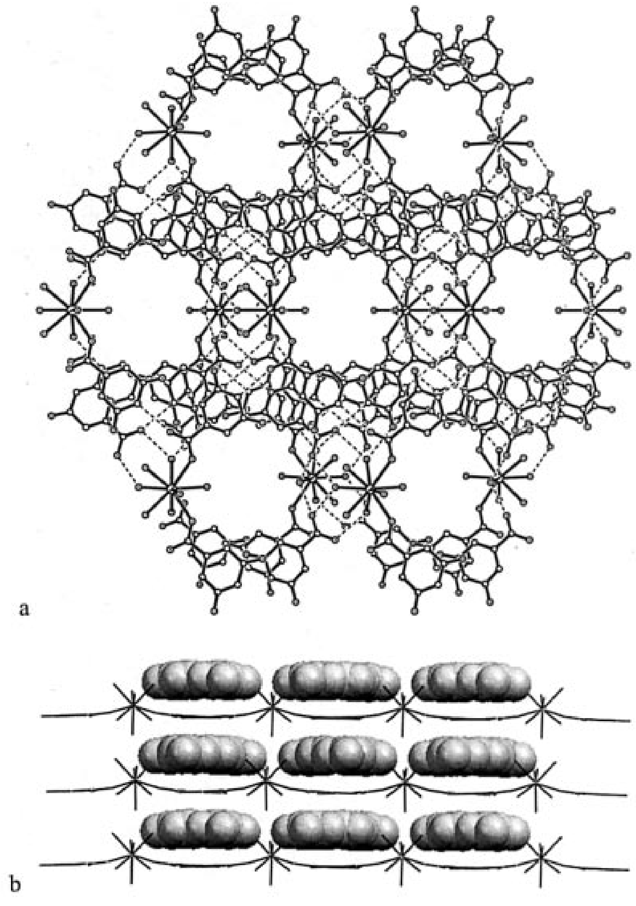


Figure 5. (a) the honeycombed structure with quasi-channels along the *c* axis for **4** and **5**, guest water molecules are omitted for clarity; (b) 3D packing structure along the *b* axis for **4** and **5**, space-filingl sphere (uncoordinated orotate ligands), wire-frame (coordinated orotate ligands)

The crystal structure of **5** is isomorphous to that of **4**; the local coordination environment around the Nd$^{III}$ ion is shown in Figure 1 (see **c**). The Nd$^{III}$ ion is nine-coordinate, with bonds to two carboxylate oxygen atoms from different orotate ligands, one oxygen atom from a hydroxyl group and six oxygen atoms from coordinated water molecules. Hydrogen bonding and π-π stacking interactions between neighboring heterocyclic rings of uncoordinated and coordinated orotate ligands, with distances from 3.22 to 3.61 Å, extend complex **5** into a honeycombed structure with unique quasi-channels accommodating guest water molecules.

It is interesting to observe the effect of the lanthanide contraction on the structures of complexes **1−5**. La$^{3+}$ forms one-dimensional, mononuclear structures and Ce$^{3+}$ also forms a one-dimensional structure. However, because of their smaller atomic sizes, Pr$^{3+}$ and Nd$^{3+}$ only form mononuclear structures. This is similar to the observation of Li and co-workers, who have reported the effect of the lanthanide contraction on crystal structure dimensions.[8a]

Complexes **6−10** are isostructural, possessing three-dimensional network structures constructed by eight-coordinate Ln$^{III}$ centers. As shown in Figure 6, the Ln$^{III}$ ion is coordinated by one nitrogen and seven oxygen atoms, of which three oxygen atoms come from OH$^-$ groups, three oxygen atoms from different orotate ligands, and one oxygen atom from a coordinated water molecule. The carboxylic group and the adjacent nitrogen of orotic acid are deprotonated during the formation of **6−10**, and each orotate ligand acts as a tetradentate ligand linking three metal atoms in a chelating-bridging mode through one carboxylate oxygen, two carbonyl oxygens and the deprotonated nitrogen ($^{d}$Hdtpc$^{2-}$, d in Scheme 1). Each hydroxyl group acts as a $\mu_3$-bridge linking three Ln$^{III}$ ions (e in Scheme 1). Orotic acid usually acts as a bidentate dianionic ligand chelating to one metal ion through the deprotonated carboxylic group and the adjacent nitrogen atom; the two carbonyl oxygen atoms usually do not engage in coordination owing to their weak coordination ability. Although several examples show the coordination of a carbonyl oxygen,[10a,23,24] at least one of them remains free. In **6−10** both carbonyl oxygen atoms engage in coordination to Ln$^{III}$, and this unusual coordination mode may be ascribed to the high affinity of lanthanide ions for oxygen.

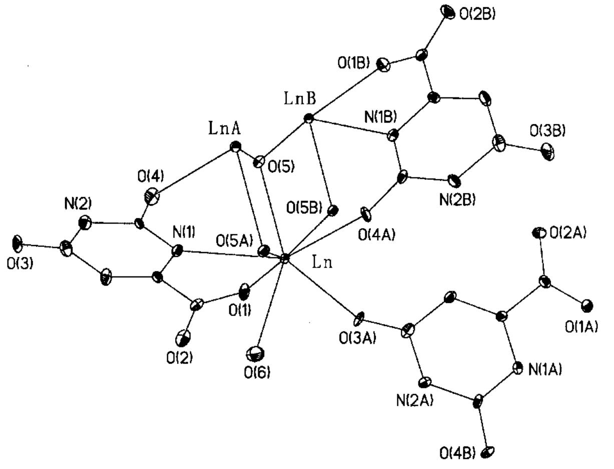


Figure 6. Local coordination environment around metal ions in **6−10**

[Ln(Hdtpc)(OH)($H_2O$)] can be viewed as the basic building block for complexes **6−10**. Every two such blocks are connected by a shared orotate ligand and a $\mu_3$-OH moiety to give rise to a zig-zag lathanide chain (Figure 7) with Ln−Ln distances of 4.0065(1) Å for **6**, 3.9117(7) Å for **7**, 3.8466(1) Å for **8**, 3.824(2) Å for **9**, and 3.752(2) Å for **10**. The chains are further joined by the remaining carbonyl oxygen of the orotate ligands in a different direction to complete the eight-coordinate environment of Ln$^{III}$, forming the final three-dimension frameworks along the *c* axis (Figure 8). In other words, the structures of **6−10** can also be regarded as ladder-like chains formed by Ln$^{III}$−OH and orotate spacers

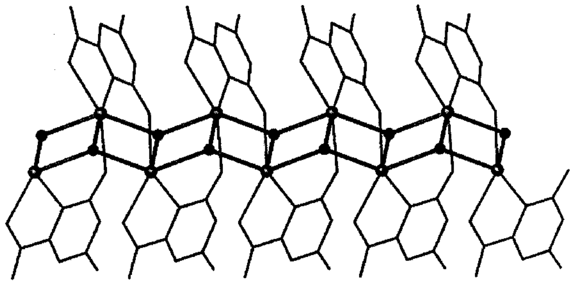


Figure 7. The zig-zag lanthanide chain formed by orotate ligands, $\mu_3$-OH bridges in **6−10**

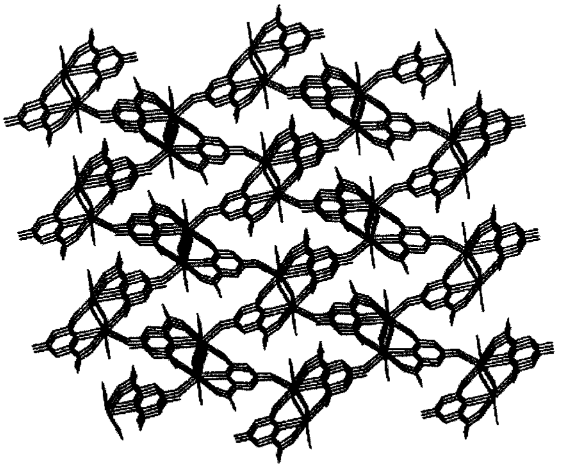


Figure 8. Packing structure along the *c* axis of **6−10**

## Conclusions

In conclusion, ten lanthanide complexes have been prepared from orotic acid and the appropriate lanthanide salt. Lanthanide complexes with different structures were isolated from aqueous solution due to the effects of the lanthanide contraction. Nevertheless, the same geometries of complexes **6−10** were obtained with the hydrothermal method, which implies that the effects of the lanthanide contraction and the solution pH on crystal formation can be ignored in Ln-orotate hydrothermal reactions. The different results between solution and hydrothermal condition may be due to their different reaction mechanisms.

## Experimental Section

### Preparation of Complexes

**General:** All chemicals were used as purchased without purification prior to reaction. The infrared spectra were recorded as KBr pellets in the 4000−400 cm$^{-1}$ region on a Magna 750 FT-IR spectrophotometer. The C, H and N microanalyses were carried out with a Perkin−Elmer 240-element analyzer in this institute.

**[{La($^{a}$H$_2$dtpc)$_2$($^{b}$H$_2$dtpc)(H$_2$O)$_4$}·H$_2$O]$_n$ (1):** A mixture of La(NO$_3$)$_3$·6H$_2$O (0.13 g, 0.3 mmol), H$_3$dtpc (0.104 g, 0.6 mmol), H$_2$O (20 mL) and EtOH (10 mL) was heated to boiling with stirring for 30 min. The solution was adjusted to pH 4−5 with 12 M aqueous NH$_4$OH and allowed to cool to room temperature. After two days colorless sheet-like crystals were obtained. Yield: 65%. $C_{15}H_{19}LaN_6O_{17}$ (694.3): calcd. C 25.95, H 2.76, N 12.11; found C 26.29, H 2.78, N 12.20. IR (KBr): $\tilde{\nu}$ = 1676 cm$^{-1}$ (vs), 1479 (m), 1431 (m), 1379 (s), 1014 (w), 928 (w), 856 (w), 773 (m), 760 (w), 546 (m), 430 (w).

**[La($^{a}$H$_2$dtpc)$_2$($^{c}$H$_2$dtpc)(H$_2$O)$_6$]·4H$_2$O (2):** A mixture of La(NO$_3$)$_3$·6H$_2$O (0.11 g, 0.25 mmol), H$_3$dtpc (0.044 g, 0.25 mmol), and H$_2$O (20 mL) was heated in a 25 mL Teflon-lined bomb at 110 °C for 3 days to yield a colorless solution (pH 4−5). After evaporation for several days at room temperature, colorless sheet-like crystals were obtained. Yield: 30%. $C_{15}H_{29}LaN_6O_{22}$ (784.3): calcd. C 22.97, H 3.73, N 10.71; found C 23.17, H 3.61, N 10.93. IR (KBr): $\tilde{\nu}$ = 1705 cm$^{-1}$ (vs), 1635 (vs), 1597 (s), 1491 (m), 1431 (m), 1373 (s), 1012 (w), 935 (w), 868 (w), 777 (w), 648 (w), 550 (m), 517 (w), 426 (w).

**[{Ce($^{a}$H$_2$dtpc)$_2$($^{b}$H$_2$dtpc)(H$_2$O)$_4$}·H$_2$O]$_n$ (3):** A mixture of Ce(NO$_3$)$_3$·6H$_2$O (0.087 g, 0.2 mmol), H$_3$dtpc (0.07 g, 0.4 mmol), H$_2$O (20 mL), and EtOH (10 mL) was heated to boiling with stirring for 30 min. The solution was adjusted to pH 4−5 with 12 M aqueous NH$_4$OH mixture and allowed to cool slowly to room temperature. After two days colorless sheet-like crystals were obtained. Yield: 60%. $C_{15}H_{19}CeN_6O_{17}$ (695.5): calcd. C 25.91, H 2.75, N 12.08; found C 26.13, H 2.68, N 12.17. IR (KBr): $\tilde{\nu}$ = 1709 cm$^{-1}$ (vs), 1628 (vs), 1439 (s), 1390 (s), 1313 (m), 1018 (w), 856 (w), 931(W), 798 (m), 559 (m), 451 (w).

**[Pr($^{a}$H$_2$dtpc)$_2$(OH)(H$_2$O)$_6$]·(H$_3$dtpc)$_2$·7H$_2$O (4):** A mixture of Pr$_2$O$_3$ (0.068 g, 0.2 mmol), H$_3$dtpc (0.14 g, 0.8 mmol), and water (30 mL) was heated to boiling with stirring for 30 min, the pH was adjusted to 3−4 by addition of 6 M aqueous H$_2$SO$_4$ and the mixture was then filtered. The filtrate was allowed to cool to room temperature. After two days light-blue crystals were obtained. Yield: 65%. $C_{20}H_{41}N_8O_{30}Pr$ (1014.5): calcd. C 23.67, H 4.07, N 11.04; found C 23.75, H 3.98, N 11.09. IR (KBr): $\tilde{\nu}$ = 1736 cm$^{-1}$ (vs), 1635 (vs), 1489 (m), 1408 (vs), 1383 (s), 1011 (w), 931 (w), 814 (m), 754 (m), 544 (s), 432 (m).

**[Nd($^{a}$H$_2$dtpc)$_2$(OH)(H$_2$O)$_6$]·(H$_3$dtpc)$_2$·7H$_2$O (5):** This complex was prepared as above by using Nd$_2$O$_3$ instead of Pr$_2$O$_3$. Yield: 65%. $C_{20}H_{41}N_8NdO_{30}$ (1017.8): calcd. C 23.60, H 4.06, N 11.01; found C 23.77, H 4.01, N 11.16. IR (KBr): $\tilde{\nu}$ = 1739 cm$^{-1}$ (vs), 1670 (vs), 1635 (vs), 1489 (m), 1410 (vs), 1383 (vs), 1011 (w), 930 (w), 818 (m), 754 (m), 544 (s), 432 (m).

**[La($^{d}$Hdtpc)(OH)(H$_2$O)]$_n$ (6):** A mixture of La$_2$O$_3$ (0.0325 g, 0.1 mmol), H$_3$dtpc (0.035 g, 0.2 mmol) and water (15 mL) was placed in a 25 mL stainless reactor fitted with a Teflon liner and heated to 160 °C for 72 hours. It was then cooled to room temperature, and colorless needle-like crystals were obtained. Yield: 80%.

$C_5H_5LaN_2O_6$ (328.0): calcd. C 18.31, H 1.54, N 8.54; found C 18.82, H 1.46, N 8.76. IR (KBr): $\tilde{\nu}$ = 1664 cm$^{-1}$ (vs), 1641 (vs), 1581 (s), 1558 (s), 1485 (m), 1407 (s), 1373 (s), 1335 (s), 1011 (m), 955 (w), 845 (m), 575 (m), 540 (w), 426 (w).

**[Nd($^d$Hdtpc)(OH)($H_2O$)]$_n$ (7):** This complex was prepared in a similar manner to **6** but with $Nd_2O_3$ instead of $La_2O_3$. Light-red crystals were obtained in 85% yield . $C_5H_5N_2NdO_6$ (333.3): calcd. C 18.02, H 1.51, N 8.40; found C 18.35, H 1.44, N 8.60. IR (KBr): $\tilde{\nu}$ = 1643 cm$^{-1}$ (vs), 1487 (m), 1412 (s), 1336 (s), 1012 (s), 957 (w), 847 (m), 806 (m), 577 (m), 430 (w).

**[Eu($^d$Hdtpc)(OH)($H_2O$)]$_n$ (8):** This complex was prepared in a similar manner to **6** but with $Eu_2O_3$ instead of $La_2O_3$. Colorless crystals were obtained in 80% yield. $C_5H_5EuN_2O_6$ (341.1): calcd. C 17.61, H 1.48, N 8.21; found C 17.36, H 1.43, N 8.34. IR (KBr): $\tilde{\nu}$ = 1672 cm$^{-1}$ (vs), 1649 (vs), 1487 (m), 1417 (s), 1340 (s), 1157 (w), 1014 (m), 958 (w), 808 (m), 771 (m), 434 (w).

**[Gd($^d$Hdtpc)(OH)(H2O)]$_n$ (9):** This complex was prepared in a similar manner to **6** but with $Gd_2O_3$ instead of $La_2O_3$. Colorless crystals were obtained in 85% yield. $C_5H_5GdN_2O_6$ (346.4): calcd. C 17.34, H 1.46, N 8.09; found C 16.97, H 1.36, N 7.79. IR (KBr): $\tilde{\nu}$ = 1674 cm$^{-1}$ (vs), 1651 (vs), 1579 (s), 1489 (m), 1417 (s), 1342 (s), 1014 (m), 958 (w), 810 (m), 579 (w), 436 (w).

**[Er($^d$Hdtpc)(OH)($H_2O$)]$_n$ (10):** This complex was prepared in a similar manner to **6** but with $Er_2O_3$ instead of $La_2O_3$. Colorless crystals were obtained in 85% yield. $C_5H_5ErN_2O_6$ (356.4): calcd. C 16.85, H 1.41, N 7.86; found C 16.93, H 1.37, N 7.95. IR (KBr): $\tilde{\nu}$ = 1655 cm$^{-1}$ (vs), 1585 (s), 1487 (m), 1421 (s), 1016 (m), 962 (w), 820 (m), 623 (m), 579 (w), 436 (w).

**X-ray Crystallography:** Single crystals of complexes **1−10** with dimensions 0.8 × 0.16 × 0.1 (**1**), 0.8 × 0.26 × 0.2 (**2**), 0.8 × 0.24 × 0.12 (**3**), 0.6 × 0.24 × 0.16 (**4**), 0.6 × 0.20 × 0.12 (**5**), 0.36 × 0.24 × 0.04 (**6**), 0.24 × 0.08 × 0.06 (**7**), 0.4 × 0.24 × 0.04 (**8**), 0.4 ×

Table 1. Crystal data for **1−5**

| Complex | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{15}H_{19}LaN_6O_{17}$ | $C_{15}H_{29}LaN_6O_{22}$ | $C_{15}H_{19}CeN_6O_{17}$ | $C_{20}H_{43}PrN_8$O31 | $C_{20}H_{43}NdN_8O_{31}$ |
| Molecular mass | 694.27 | 784.35 | 695.48 | 1014.49 | 1017.82 |
| Crystal system | triclinic | triclinic | triclinic | orthorhombic | orthorhombic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | *Cmc*2 (1) | *Cmc*2 (1) |
| *a* (Å) | 8.5991(5) | 6.7944(2) | 8.5414(17) | 22.9991(17) | 22.9997(6) |
| *b* (Å) | 10.2849(6) | 10.1432(2) | 10.260(2) | 12.7674(4) | 12.7520(4) |
| *c* (Å) | 13.4175(8) | 20.5961(6) | 13.335(3) | 12.6962(4) | 12.6996(3) |
| $\alpha$ (°) | 90.914(10) | 94.731(10) | 90.95(3) | 90 | 90 |
| $\beta$ (°) | 99.77(3) | 93.44(10) | 100.27(3) | 90 | 90 |
| $\gamma$ (°) | 105.69(10) | 105.523 | 105.89(3) | 90 | 90 |
| *V* (Å$^3$) | 1123.48(11) | 1358.00(6) | 1103.3(4) | 3728.1(2) | 3724.69(18) |
| *Z* | 2 | 2 | 2 | 4 | 4 |
| $D_c$ (g·cm$^{-3}$) | 2.052 | 1.918 | 2.094 | 1.840 | 1.847 |
| $\mu$ (mm$^{-1}$) | 2.003 | 1.682 | 2.167 | 1.429 | 1.516 |
| *F*(000) | 688 | 788 | 690 | 2104 | 2108 |
| $2\theta$ range (°) | 1.54−25.10 | 1.00−25.02 | 1.56−27.51 | 1.77−25.09 | 1.77−25.04 |
| *R*1 [$I > 2\sigma(I)$] | 0.0379 | 0.0380 | 0.0248 | 0.0318 | 0.0372 |
| *R*1 (all data) | 0.0440 | 0.0461 | 0.0303 | 0.0334 | 0.0460 |
| *S* ($F^2$) | *1.053* | *1.082* | *1.221* | *1.059* | *1.068* |

Table 2. Crystal data for **6−10**

| Complex | **6** | **7** | **8** | **9** | **10** |
|---|---|---|---|---|---|
| Empirical formula | $C_5H_5LaN_2O_6$ | $C_5H_5NdN_2O_6$ | $C_5H_5EuN_2O_6$ | $C_5H_5GdN_2O_6$ | $C_5H_5ErN_2O_6$ |
| Molecular mass | 328.02 | 333.35 | 341.07 | 346.36 | 356.37 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| Space group | *Pna*2 (1) | *Pna*2 (1) | *Pna*2 (1) | *Pna*2 (1) | *Pna*2 (1) |
| *a* (Å) | 10.2210(16) | 10.1518(13) | 10.893(15) | 10.654(10) | 10.004(7) |
| *b* (Å) | 16.976(3) | 16.763(2) | 16.575(5) | 16.5208(17) | 16.310(8) |
| *c* (Å) | 4.6996(17) | 4.6564(6) | 4.6334(7) | 4.6223(5) | 4.598(3) |
| $\beta$ (°) | 90 | 90 | 90 | 90 | 90 |
| *V* (Å$^3$) | 815.5(3) | 792.39(17) | 774.9(2) | 768.64(14) | 750.2(8) |
| *Z* | 4 | 4 | 4 | 4 | 4 |
| $D_c$ (g·cm$^{-3}$) | 2.672 | 2.794 | 2.924 | 2.993 | 3.155 |
| $\mu$ (mm$^{-1}$) | 5.246 | 6.560 | 8.102 | 8.636 | 11.194 |
| *F*(000) | 616 | 628 | 640 | 644 | 660 |
| $2\theta$ range (°) | 2.33−25.96 | 2.35−25.01 | 2.36−25.02 | 2.37−25.07 | 2.39−25.13 |
| *R*1 [$I > 2\sigma(I)$] | 0.0375 | 0.0298 | 0.0441 | 0.0506 | 0.0476 |
| *R*1 (all data) | 0.0523 | 0.0344 | 0.0626 | 0.0752 | 0.0665 |
| *S* ($F^2$) | 1.066 | 1.091 | 1.020 | 1.036 | 1.019 |

0.36 × 0.04 (**9**), 0.24 × 0.05 × 0.03 mm$^3$ (**10**) were selected for crystal structure analyses. Data collection for complexes **1−5** and **7−10** was performed at 293 K on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program. Data collection for **6** was performed at 293 K on a CAD4 four-cycle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073Å). Corrections for Lorentz polarization factors and empirical absorption were applied to the data. The structures of **1−10** were solved by direct methods; the heavy atoms were located from the E-maps; other non-hydrogen atoms were derived from the successive difference Fourier syntheses. All non-hydrogen atoms were refined by full-matrix, least-squares minimizations of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for **1−5** and **7**. The metal atoms were refined anisotropically while all other non-hydrogen atoms were refined isotropically for **6**, **8**, **9** and **10** in order to obtain a reasonable data/parameter ratio. One free water molecule (O14) in **4** and **5** was disordered over two sets of positions refined with restraints. The calculations were performed with the SHELXTL-97 program package.[29] The hydrogen atoms were located from the difference Fourier map and refined isotropically. Table 1 summarizes the important crystal data for **1−5** and Table 2 the data for **6−10**. The selected bond lengths and angles for **1−10** are provided in Table S1 in the Supporting Information.

CCDC-202618−202627 (for **1−10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

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