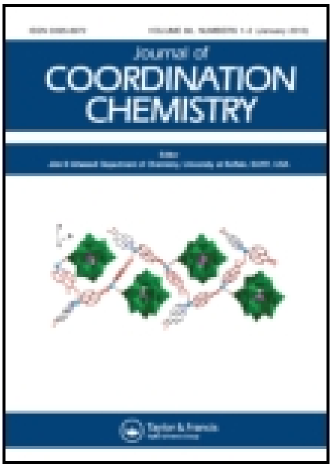
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:25
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



CrossMark
Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Lanthanide contraction in linear lanthanide-oxygen clusters

Xin Fang[a], Li-Mao Cai[a], Yu-Chen Shao[a] & Mei-Jin Lin[a]
[a] College of Chemistry, Fuzhou University, Fuzhou, PR China

Accepted author version posted online: 26 Sep 2014.Published online: 14 Oct 2014.

To cite this article: Xin Fang, Li-Mao Cai, Yu-Chen Shao & Mei-Jin Lin (2014) Lanthanide contraction in linear lanthanide-oxygen clusters, Journal of Coordination Chemistry, 67:21, 3542-3550, DOI: 10.1080/00958972.2014.969723

To link to this article: http://dx.doi.org/10.1080/00958972.2014.969723

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

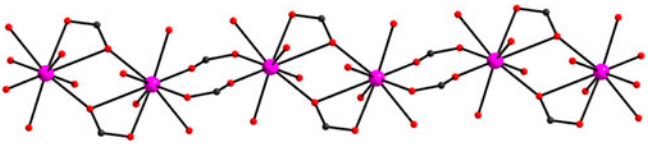
Journal of Coordination Chemistry, 2014
Vol. 67, No. 21, 3542–3550, http://dx.doi.org/10.1080/00958972.2014.969723

Lanthanide contraction in linear lanthanide–oxygen clusters

XIN FANG, LI-MAO CAI, YU-CHEN SHAO and MEI-JIN LIN*

College of Chemistry, Fuzhou University, Fuzhou, PR China

(*Received 9 June 2014; accepted 26 August 2014*)



Hydrothermal reactions of substituted phthalic acid with lanthanide salts lead to two kinds of coordination polymers containing linear lanthanide–oxygen clusters, where the different coordination patterns are attributed to the effect of lanthanide contraction.

Five coordination polymers containing linear lanthanide–oxygen clusters **1–5** have been synthesized by a hydrothermal reaction of 3-(quinolin-8-yloxy) phthalic acid (H_2L) with the respective lanthanide salt. The X-ray single crystal structural analyses revealed that these five crystalline materials belong to two isostructures with formulas $[LnHL_2(H_2O)_2]_n$ (**Ln1**, where Ln = La **1**, Ce **2**, Pr **3**) and $[Ln(HL)(L)(H_2O)]_n$ (**Ln2**, where Ln = Nd **4**, Sm **5**), respectively, which are attributed to the effect of lanthanide contraction. In both structures, the lanthanide cations were bridged by two carboxyl groups of L^{2-} through Ln–O bonds to form 1-D linear lanthanide–oxygen clusters, which were further connected by intermolecular π–π stacking interactions between quinolinyl units to generate 3-D supramolecular polymers with moderate luminescence and high thermal stability.

Keywords: Coordination polymers; Oxygen clusters; Lanthanide complexes; Lanthanide contraction

1. Introduction

Coordination polymers have received attention for interesting structures [1] and potential applications, such as magnetism [2], luminescence [3], gas storage and separation [4], catalysis [5], and non-linear optics (NLO) [6]. Lanthanide compounds always exhibit extraordinary luminescent and magnetic properties [7], which strongly stimulates our interest in exploring new lanthanide–containing coordination polymers, particularly those using the aromatic carboxylate ligands with large porosity.

As multidentate O-donor ligands, *para*- and *meta*-benzene dicarboxylate are common building blocks used for construction of lanthanide–containing coordination polymers [8]. However, only a few examples with *ortho*-benzene dicarboxylate (phthalic acid) have been

---

*Corresponding author. Email: meijin_lin@fzu.edu.cn reported [9]. Owing to the small bridging angles between two carboxylate groups and thus steric congestion, most of the available structures from phthalic acid derivatives are 1- and 2-D [10]. In order to increase their dimensions, the common strategy is use of N-donor ligands to further connect the generated low-dimensional subunits, which seems impolitic due to the multicomponent self-assembly [11]. Alternatively, it is easy to visualize that the same ends can be reached through the incorporation of N-donor group into phthalic acid through organic synthesis. To our surprise, so far no example has been found in Cambridge Structure Database. Herein, we introduced a quinoline moiety into phthalic acid at the 3-position and anticipated increasing the low dimensional polymers by coordination or π–π interaction. The basicity of quinoline and the acidity of carboxylic acid also favor pH by controlling the hydrothermal reaction. As expected, five lanthanide–containing 3-D supramolecular coordination polymers with 1-D linear lanthanide–oxygen clusters in different coordination pattern were obtained by intermolecular π–π interactions between quinolinyl units, wherein the different coordination patterns are attributed to the effect of lanthanide contraction.

2. Experimental

2.1. *Materials and measurements*

Potassium carbonate (≥99%), 8-hydroxyquinoline, potassium hydroxide (KOH, analytical reagent grade), and DMF (analytical reagent grade) were obtained from commercial suppliers. All chemicals and reagents were used as received unless otherwise stated. The starting material 3-nitropthalonitrile was prepared according to the literature [12]. Flash column chromatography was performed using silica gel (Si60, mesh size 45–75 μm). NMR spectra were recorded with a Bruker Avance 400 MHz instruments. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^{1}H coupling constants J are given in Hertz (Hz). ESI mass spectra were recorded on a Thermo Finnigan DECAX-30,000 LCQ Deca XP spectrometer. IR spectra were recorded from 4000 to 400 cm^{-1} on a Perkin Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. Fluorescence spectra were measured on an Edinburgh Instrument FL/FS-920 fluorescence spectrometer. Thermal analyses were performed on a SDT Q600 instrument from room temperature to 1000 °C with a heating rate of 10 °C min^{-1} under nitrogen.

2.2. *Synthesis of 3-(quinolin-8-yloxy) phthalic acid (H_2L) [13]*

As shown in scheme 1, under nitrogen, 1.73 g (10.0 mM) 3-nitropthalonitrile, 1.45 g (10.0 mM) 8-hydroxyquinoline, and 4.14 g (30.0 mM) K_2CO_3 were suspended in 20 mL dry DMF and stirred at room temperature for 4 h. Then the reaction mixture was poured into water (200 mL) and the solid material was separated by filtration. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as an eluent. After removal of the solvent with a rotary evaporator, 2.25 g yellow 3-(quinolin-8-yloxy)-phthalonitrile was obtained in a yield of 83%. M.p. 205–206 °C; IR/cm^{-1} (KBr): 2226(m), 1588(m), 1501(m), 1464(m), 1290(s), 791(m), 763(m); ^{1}H NMR (400 MHz, δ, DMSO-d$_6$): 8.85–8.84 (dd, J_1 = 4.10 Hz, J_2 = 1.50 Hz, 1H), 8.53–8.51 (dd, J_1 = 8.40 Hz, J_2 = 1.50 Hz, 1H), 8.05–8.02 (dd, J = 8.00 Hz, J_2 = 1.40 Hz, 1H), 7.79–7.71 (m, *3*H), 7.68–7.61 (m, *2*H), 6.95–6.93 (d, J = 8.40 Hz, 1H).

Under nitrogen, 2.71 g (10.0 mM) 3-(quinolin-8-yloxy) phthalonitrile and 1.20 g (30.0 mM) KOH were suspended in 30 mL distilled water and refluxed until the solution turned clear. After being cooled to room temperature, the pH of the reaction mixture was slowly adjusted to 5–6 with HCl (6.0 M L^{-1}) under stirring. The solid material was separated by filtration and then washed successively with water (3 × 30 mL). After drying in vacuum, 2.78 g of H_2L was obtained in a yield of 91%. M.p. 197.8–198.6 °C; ESI-MS: *m/z*, Calcd 309.27(M), found 308.5 (M^-, 100%); IR/cm^{-1} (KBr): 3585(m), 1743(s), 1598(m), 1455 (m), 1416(m), 1244(s), 834(m), 772(m). ^{1}H NMR (400 MHz, δ, DMSO-d_6): 13.26 (bs, 2H), 8.91–8.89 (dd, $J_1 = 4.10$ Hz, $J_2 = 1.60$ Hz, 1H), 8.47–8.44 (dd, $J_1 = 8.40$ Hz, $J_2 = 1.60$ Hz, 1H). 7.85–7.82 (dd, $J_1 = 8.20$ Hz, $J_2 = 1.00$ Hz, 1H), 7.67–7.59 (m, 3H), 7.42–7.38 (m, $J_1 = 8.00$ Hz, 1H), 7.30–7.28 (dd, $J_1 = 7.60$ Hz, $J_2 = 1.10$ Hz,1H), 6.95–6.92 (dd, $J_1 = 8.20$ Hz, $J = 0.80$ Hz, 1H). ^{13}C NMR (400 MHz, δ, DMSO-d_6): δ 166.84 (C), 166.32 (C), 152.29 (C), 149.67 (C), 147.41 (CH), 143.45 (C), 133.03 (CH), 130.82 (C),130.70 (CH), 129.72 (C),129.24 (CH), 129.05 (CH), 126.12 (CH), 124.23 (CH), 123.61 (CH), 122.95 (C), 118.82 (CH).

2.3. *Synthesis of lanthanide coordination polymers 1–5*

A mixture containing 0.10 mM lanthanide salts (25.0 mg $LaCl_3 \cdot 6H_2O$, 40.4 mg $Ce_2(SO_4)_3 \cdot 4H_2O$, 25.0 mg $PrCl_3 \cdot 6H_2O$, 33.0 mg $Nd(NO_3)_3 \cdot xH_2O$ or 24.7 mg $Sm(NO_3)_3$), 31.0 mg H_2L (0.10 mM), 8.0 mg NaOH (0.20 mM), and 5 mL H_2O was sealed in a 23 mL Teflon-lined stainless steel reactor and heated to 150 °C for four days, then cooled at 6 °C h^{-1} to room temperature. The crystals were separated by filtration and dried under air in a yield based on Ln cations of 80, 85, 90, 79, and 75% for **1–5**, respectively.

2.3.1. $[LaHL_2(H_2O)_2]_n$ (1). IR/cm^{-1} (KBr), 3351(m), 3053(m), 1600(m), 1547(vs), 1467(m), 1400(vs), 1333(m), 1253(s), 1092(m), 815(s), 770(s), 690(s).

2.3.2. $[CeHL_2(H_2O_2)]_n$ (2). IR/cm^{-1} (KBr), 3340(m), 3017(w), 1594(m), 1544(vs), 1463(m), 1398(vs), 1333(m), 1253(s), 1090(m), 811(s), 770(s), 687(s).

2.3.3. $[PrHL_2(H_2O)_2]_n$ (3). IR/cm^{-1} (KBr), 3304(m), 3017(w), 1603(m), 1540(vs), 1464(m), 1400(vs), 1333(m), 1256(s), 1090(m), 811(s), 770(s), 687(s).

2.3.4. $[Nd(HL)(L)(H_2O)_2]_n$ (4). IR/cm^{-1} (KBr), 3310(m), 3071(w), 1620(m), 1541(vs), 1469(m), 1400(vs), 1333(m), 1253(s), 1090(m), 809(s), 767(s), 687(s).

2.3.5. $[Sm(HL)(L)(H_2O)_2]_n$ (5). IR/cm^{-1} (KBr), 3309(m), 3089(w), 1623(m), 1540(vs), 1464(m), 1401(vs), 1333(m), 1250(s), 1093(m), 814(s), 770(s), 687(s).

2.4. *X-ray crystallography*

Crystal data for **1–5** were collected on a Rigaku Saturn 724 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The

Table 1. Crystallographic data and structure refinement details for **1**–**5**.

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	La($C_{17}H_9NO_5$) H_2O	Ce($C_{17}H_9NO_5$) H_2O	Pr($C_{17}H_9NO_5$) H_2O	Nd($C_{17}H_9NO_5$) H_2O	Sm($C_{17}H_9NO_5$) H_2O
Formula weight	785.41	818.62	787.41	2201.38	800.89
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*P21/c*	*P21/c*
a (Å)	26.571(5)	26.574(5)	26.53(2)	9.4033(7)	9.401(8)
b (Å)	11.675(2)	11.640(2)	11.615(8)	11.5820(8)	11.570(8)
c (Å)	9.4015(19)	9.3905(19)	9.406(8)	26.5105(11)	27.44(3)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	94.23(3)	94.36(3)	94.284(12)	94.271(12)	105.63(12)
γ (°)	90.00	90.00	90.00	90.00	90.00
Volume (Å^3)	2909.6(9)	2896.3(9)	2890.0(4)	2879.2(3)	2874(4)
Crystal size (mm)	0.37 × 0.28 × 0.20	0.57 × 0.20 × 0.18	0.23 × 0.13 × 0.11	0.36 × 0.10 × 0.10	0.68 × 0.50 × 0.23
Z	4	4	4	4	4
D_{Calcd} (g cm^{-3})	1.794	1.877	1.810	5.078	1.851
μ (Mo Kα) (mm^{-1})	1.55	1.66	1.76	21.24	2.12
F (0 0 0)	1556	1624	1564	3856	1592
θ min, max (°)	3.5, 27.6	3.5, 27.5	3.5, 27.5	3. 1, 27.5	3.1, 27.5
Total/uniques	11,571/3322	10,852/3274	11,821/3316	23,615/6595	22,638/6559
R_{int}	0.065	0.032	0.0507	0.049	0.037
Observed	3225	3219	3017	6155	6231
Restraints/parameters	0/221	2/230	2/230	0/450	0/446
GOF on F^2	1.339	1.046	1.070	1.187	1.099
R_1, wR_2 ($I > 2\sigma$)	0.0588, 0.1424	0.0285, 0.0676	0.0608, 0.1188	0.0482, 0.0824	0.0315/0.0756
R_1, wR_2 (all data)	0.0612, 0.1439	0.0291, 0.0680	0.0681, 0.1231	0.0538, 0.0845	0.0338/0.0756

structures were solved by the direct method and difference Fourier syntheses. All calculations were performed by full-matrix least-squares on F^2 using SHELX-97 [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogens were fixed at calculated positions and refined in a riding mode. Crystal data and the structure refinements are summarized in table 1. Selected bond lengths and angles of these compounds are listed in table S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.969723).

3. Results and discussion

3.1. *Synthesis*

As stated above, due to the conformational effect, the convergent phthalic acids have been reported to form lower dimensional coordination polymers. In order to increase their dimensions, a quinoline unit was incorporated into phthalic acid at the 3-position, which was anticipated to offer either additional coordination sites for lanthanide or a large π-system for π-stacking interactions. As depicted in scheme 1, a facile nucleophilic substitution of 3-nitrophthalonitrile with excess 8-hydroxyquinoline under basic conditions afforded 3-(quinolin-8-yloxy)-phthalonitrile, which is further saponificated to give the target 3-(quinolin-8-yloxy) phthalic acid (H_2L) in a yield of 75%. The chemical structure of H_2L was assigned by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy as well as MALDI-TOF mass spectroscopy (figures S1–S4 in Supplementary material).

The hydrothermal synthesis of H_2L with equal amount of five lanthanides (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+}) salts under basic conditions afforded five crystals. Although the five lanthanide cations have close electronic configurations, the single-crystal structural analyses revealed that their structural features are slightly different and thus could be divided into two categories with formulas $[LnHL_2(H_2O)_2]_n$ (**Ln1**, where Ln = La **1**, Ce **2**, Pr **3**) and $[Ln(HL)(L)(H_2O)]_n$ (**Ln2**, where Ln = Nd **4**, Sm **5**), respectively.

3.2. *Crystal structures of $[LnHL_2(H_2O)_2]_n$ (Ln1) (Ln = La 1, Ce 2, Pr 3)*

For the compounds from La^{3+}, Ce^{3+}, and Pr^{3+} that have relatively large ionic radii, the X-ray structural analyses revealed they are isostructural (monoclinic, space group *C2/c*) with only a little difference in bond lengths and bond angles (for details, see table S1 in Supplementary material). In the structures, except for the coordination waters and counter-cation H^+, no other free solvent molecules are observed. Due to the fact that coordination water molecules, carboxyl groups of H_2L and N in the latter could accept the counter-cation H^+, it could not be fixed and thus not given in the resolved structures.

For all three cases, the three components system composed of L^{2-}, Ln^{3+} (La^{3+}, Ce^{3+} or Pr^{3+}), and coordination water leads to 3-D anionic supramolecular architectures (figure 1). Lanthanide cations prefer to interact with O-donors rather than N-donors; only carboxyl groups connect to Ln^{3+} in the structures and quinolinyl groups are free. In each L^{2-}, two kinds of coordination patterns are observed for two carboxyl groups [figure 1(a)]. One acts as a μ_2-$\eta^1:\eta^1$-bridging unit to connect the neighboring two Ln^{3+} cations by two Ln–O bonds, while the other serves as a monodentate unit to coordinate to Ln^{3+}. Each Ln^{3+} cation adopts dodecahedral coordination geometry and is capped by two coordination water

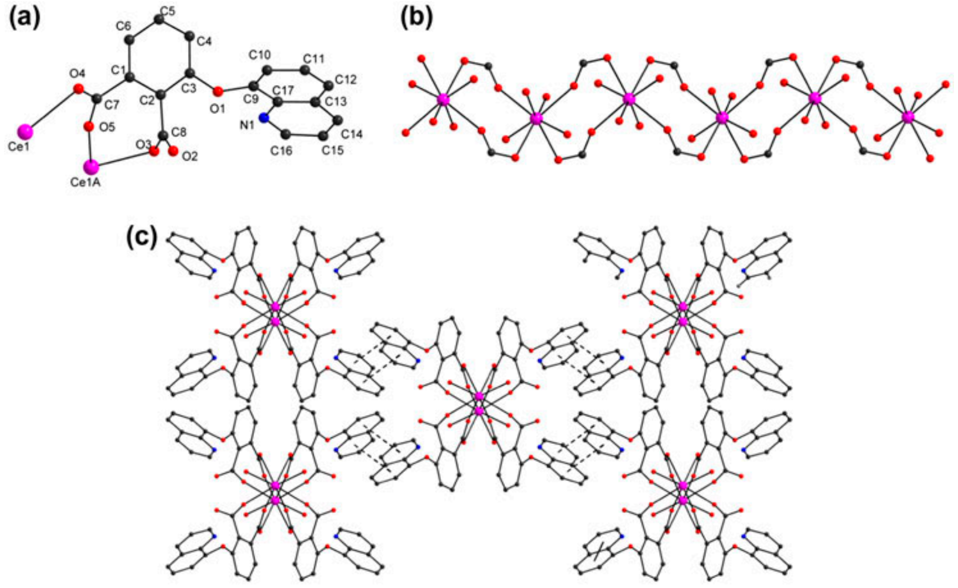


Figure 1. (a) Coordination environment for Ce(III) in **2**. Hydrogens are omitted for clarity. Symmetry codes: (A) $-x$, $-y$, $2-z$. (b) 1-D chain structure of **2**. (c) 3-D supramolecular structure of **2** formed through π–π stacking interactions.

molecules ($d_{\text{Ln–O}} = 2.47$–2.50 Å) and two oxygens from two monodentate carboxylates ($d_{\text{Ln–O}} = 2.51$–2.59 Å) and is then bridged by four oxygens from four μ_2-$\eta^1:\eta^1$-bridging carboxylates ($d_{\text{Ln–O}} = 2.51$–2.58 Å) to form an anionic 1-D network along the *c* axis with Ln–Ln distance of 4.79–4.80 Å [figure 1(b)]. The latter is further stacked by the intermolecular π–π stacking interactions (3.58 Å) between quinolinyl groups to generate the final 3-D supramolecular architectures [figure 1(c)].

3.3. *Crystal structures of [Ln(HL)(L)(H_2O)]$_n$ (Ln2) (Ln = Nd 4, Sm 5)*

Compounds **4** and **5** from Nd^{3+} and Sm^{3+} cations of small ionic radius are the second group of isostructural crystals (monoclinic, space group *P21/c*) with a formula of [Ln(HL)(L)(H_2O)]$_n$. Unlike **1–3**, the protons in **4** and **5** have very definite positions, fixed on the nitrogens of quinolinyl groups.

Although both **4** and **5** are 3-D supramolecular polymers composed of 1-D lanthanide coordination networks connected by intermolecular π–π stacking interactions between quinolinyl units [figure 2(c)], either the coordination geometries for Ln^{3+} or the coordination patterns for L^{2-} in both structures are different from those in **1–3**. As shown in figure 2(a), two coordination patterns for L^{2-} could be observed. Besides one that adopts the similar coordination pattern as in **1–3** with one carboxyl as a μ_2-$\eta^1:\eta^1$-bridging unit and the other

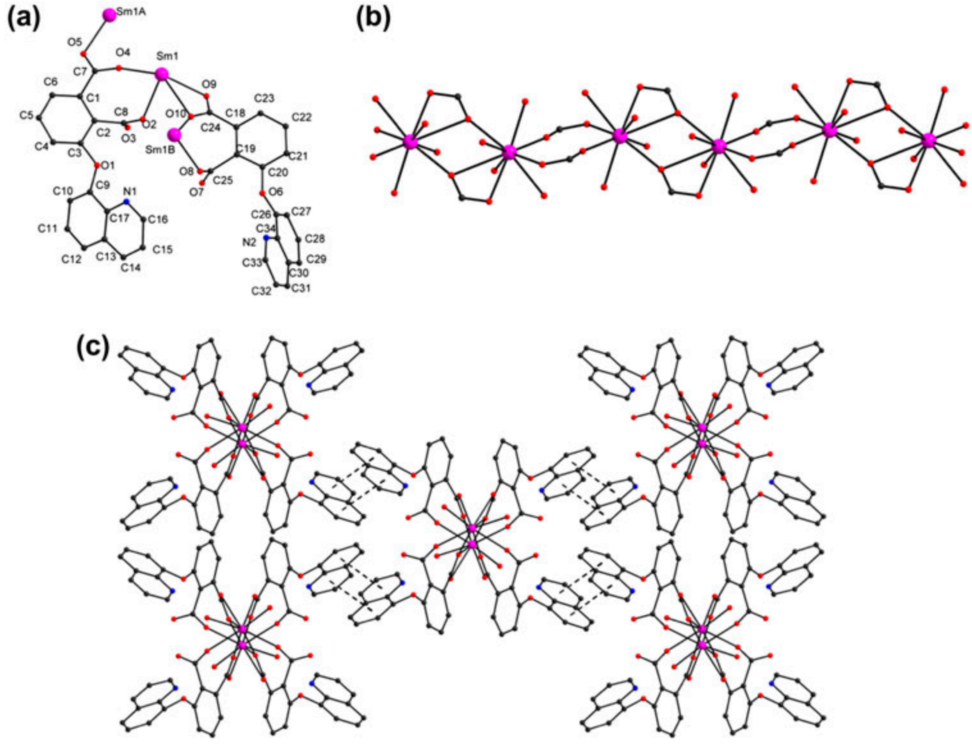
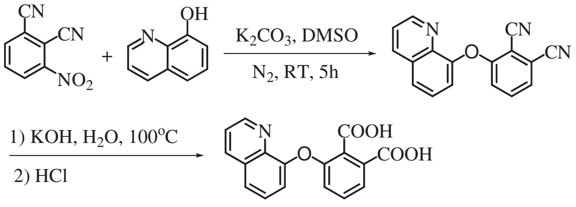


Figure 2. (a) Coordination environment for Sm(III) in **5**. Hydrogens are omitted for clarity. Symmetry codes: (A) $3-x$, $-1-y$, $-z$, (B) $2-x$, $-1-y$, $-z$. (b) 1-D chain structure of **5**. (c) The 3-D supramolecular structure of **5** formed through π–π stacking interactions.



Scheme 1. Synthesis of H_2L.

as a monodentate unit, there is the second organic L^{2-} with one carboxyl monodentate and the other one as a μ_3-$\eta^2:\eta^1$-bridging unit. In the latter bridging unit, one O is coordinated to Ln^{3+} (d_{Ln-O} = 2.51–2.53 Å), while the second bridges the neighboring two Ln^{3+} cations through Ln–O bonds (d_{Ln-O} = 2.47–2.82 Å). The coordination number for each Ln^{3+} in the structures of **4** and **5** is increased to 9 and thus it adopts a distorted tricapped trigonal prismatic coordination geometry. More specifically, the neighboring two Ln^{3+} cations, which are already capped by two oxygens from two coordination waters (d_{Ln-O} = 2.36–2.61 Å) and two oxygens from two monodentate carboxylates (d_{Ln-O} = 2.43–2.48 Å), are interconnected by two μ_3-$\eta^2:\eta^1$-bridging carboxylate groups to form a bimetallic Ln–Ln dimer ($d_{Ln\text{-}Ln}$ = 4.52–4.58 Å), which is further stringed together by two μ_2-$\eta^1:\eta^1$-bridging carboxylate groups to afford a 1-D neutral network along the *c* axis with a distance between the consecutive Ln^{3+} cations in the neighboring two bimetallic dimers of 5.02–5.07 Å [figure 2(b)]. Similar to **1–3**, the π–π stacking interactions (3.58–3.61 Å) between quinolinyl groups in neighboring 1-D coordination networks leads to a 3-D supramolecular polymer [figure 2(c)].

The different coordination patterns of Ln^{3+} in **4** and **5** from those in **1–3** may result from the increase in the effective nuclear charge number for the Nd^{3+} and Sm^{3+}, which leads to the well-known lanthanide contraction and also more accepting ability of electrons from the outer coordination ligands. Such effects were already described for the 2- or 3-D lanthanide–containing coordination polymers from other carboxyl acid derivatives [15].

3.4. *Powder X-ray diffraction, thermogravimetric analysis, and fluorescent properties*

The homogeneity of the crystalline materials **1–5**, obtained by manual separation of crystals and the powder in the mixture, was investigated by powder X-ray diffraction (figure S5). The match between the calculated and measured patterns indicated that all five crystalline materials were pure phases.

The thermal stability of **1–5** was investigated by thermogravimetric analysis measurements under nitrogen (figure S6) which revealed **1–5** lost weight at 180 °C and did not terrace even at 1000 °C. Lanthanide complexes are known for their excellent fluorescent

Table 2. Emission properties of lanthanide coordination polymers at room temperature.

Compounds	1	2	3	4	5
$\lambda_{excitation}$ (nm)	396	440	397	395	453
$\lambda_{emission}$ (nm)	480	473	478	483	504

properties. As expected, all five coordination polymers **1–5** exhibited strong solid state emission at room temperature (figure S7, table 2) and only slight difference between their emission maxima were observed. Unfortunately, no discernible effect of lanthanide contraction on their thermal stabilities and fluorescent properties could be concluded.

4. Conclusion

We have demonstrated a series of coordination polymers containing linear lanthanide–oxygen clusters from five different lanthanide ions and the 3-(quinolin-8-yloxy) phthalic acid. Due to the increasing effective nuclear charge number, the structures for Nd^{3+} and Sm^{3+} are slightly different from those from La^{3+}, Ce^{3+}, and Pr^{3+} not only in coordination geometries of metal ions but also in the coordination patterns of the organic building blocks. Imposed by the convergent conformation of reactant phthalic acid, all five structures could also be regarded as 1-D lanthanide–oxygen clusters interconnected by π–π interactions and the former is very interesting for the design of magnetic and catalytic materials. In addition, the formed 1-D coordination chains containing the free quinoline units may also be used as metallatectons for the construction of other functional metal–organic frameworks by coordinating with transition metal ions, which is under progress.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-804392, 831626, 831368, 865213, and 830805 for **1–5**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank Prof Chang-Cang Huang and Prof Jun-Dong Wang for their useful discussions.

Funding

This work has been supported by National Natural Science Foundation of China [grant number 21202020]; Doctoral Fund of Ministry of Education of China [grant number 20123514120002]; Natural Science Foundation of Fujian Province [grant number 2014J01040]; and Science & Technical Development Foundation of Fuzhou University [grant number 2012-XQ-10], [grant number 2013-XQ-14].

References

[1] (a) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **31**, 474 (1998); (b) S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000); (c) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001); (d) L. Carlucci, G. Ciani, D.M. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2003); (e) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003); (f) L. Brammer. *Chem. Soc. Rev.*, **33**, 476 (2004); (g) R.J. Hill, D.L. Long, N.R. Champness, P. Hubberstey, M. Schroder. *Acc. Chem. Res.*, **38**, 337 (2005).

[2] (a) B.Q.Ma, D.S.Zhang, S.Gao, T.Z.Jin, C.H.Yan, G.X. Xu. *Angew. Chem., Int. Ed.*, 39, 3644 (2000); (b) F.-C. Liu, Y.-F. Zeng, J.-R. Li, X.-H. Bu, J. Ribas, S.R. Batten. *Inorg. Chem.*, **45**, 6129 (2006); (c) S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003).

[3] (a) Z.T. Yu, G.H. Li, Y.S. Jiang, J.J. Xu, J.S. Chen. *Dalton Trans.*, **22**, 4219 (2003); (b) A.P. Bassett, S.W. Magennis, P.B. Glover, D.J. Lewis, N. Spencer, S. Parsons, R.M. Williams, L.D. Cola, Z. Pikramenou. *J. Am. Chem. Soc.*, **126**, 9413 (2004); (c) Y.-Q. Sun, J. Zhang, Y.-M. Chen, G.-Y. Yang. *Angew. Chem., Int. Ed.*, **44**, 5814 (2005); (d) J. Yang, Q. Yue, G.-D. Li, J.-J. Cao, G.-H. Li, J.-S. Chen. *Inorg. Chem.*, **45**, 2857 (2006).

[4] (a) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa. *Angew. Chem., Int. Ed.*, **42**, 428 (2003); (b) J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi. *J. Am. Chem. Soc.*, **126**, 5666 (2004); (c) J.L.C. Rowsell, O.M. Yaghi. *Angew. Chem., Int. Ed.*, **44**, 4670 (2005).

[5] (a) Z.-T. Yu, Z.-L. Liao, Y.-S. Jiang, G.-H. Li, J.-S. Chen. *Chem. Eur. J.*, **11**, 2642 (2005); (b) D.N. Dybtsev, A.L. Nuzhdin, H. Chun, K.P. Bryliakov, E.P. Talsi, V.P. Fedin, K. Kim. *Angew. Chem., Int. Ed.*, **45**, 916 (2006); (c) A.E. PlateroPrats, V.A. de la Peña-O'Shea, M. Iglesias, N. Snejko, A. Monge, E. Gutiérrez-Puebla. *ChemCatChem*, **2**, 147 (2010).

[6] (a) J. Long, O.M. Yaghi. *Chem. Soc. Rev.*, **38**, 1213 (2009); (b) S. Couck, J.F.M. Denayer, G.V. Baron, T. Rémy, J. Gascon, F. Kapteijn. *J. Am. Chem. Soc.*, **131**, 6326 (2009); (c) K. Li, D.H. Olson, J. Seidel, T.J. Emge, H. Gong, H. Zeng, J. Li. *J. Am. Chem. Soc.*, **131**, 10368 (2009); (d) K.-F. Wang, S. Miao, W.-H. Sun. *Dalton Trans.*, 4085 (2009); (e) T. Liu, Y.-J. Zhang, Z.-M. Wang, S. Gao. *J. Am. Chem. Soc.*, **130**, 10500 (2008).

[7] (a) K. Junji, O.M. Yaghi. *Chem. Rev.*, **102**, 2357 (2002); (b) N.M. Shavaleev, G. Accorsi, D. Virgili, Z.R. Bell, T. Lazarides, G. Calogero, N. Armaroli, M.D. Ward. *Inorg. Chem. Commun.*, **44**, 61 (2005); (c) C.L. Cahill, D.T. Lill, M. Frisch. *CrystEngComm*, **9**, 15 (2007); (d) D.T. de Lill, A. de Bettencourt-Dias, C.L. Cahill. *Inorg. Chem.*, **46**, 3960 (2007); (e) J. Xu, J.-W. Cheng, W.-P. Su, M.-C. Hong. *Cryst. Growth Des.*, **11**, 2294 (2011).

[8] (a) A. Deluzet, W. Maudez, C. Daiguebonne, O. Guillou. *Cryst. Growth Des.*, **3**, 475 (2003); (b) C. Daiguebonne, N. Kerbellec, O. Guillou, J.C. Bünzli, F. Gumy, L. Catala, T. Mallah, N. Audebrand, Y. Gérault, K. Bernot, G. Calvez. *Inorg. Chem.*, **47**, 3700 (2008); (c) D.X. Hu, F. Luo, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **7**, 1733 (2007); (d) A. Bettencourt-Dias. *Inorg. Chem.*, **44**, 2734 (2005); (e) L.-P. Zhang, Y.-H. Wan, L.-P. Jin. *Polyhedron*, **22**, 981 (2003); (f) C. Serre, F. Millange, J. Marrot, G. Férey. *Chem. Mater.*, **14**, 2409 (2002).

[9] (a) Y. Wan, L. Jin, K. Wang, L. Zhang, X. Zheng, S. Lu. *New J. Chem.*, **26**, 1590 (2002); (b) A. Thirumurugan, S. Natarajan. *J. Mater. Chem.*, **15**, 4588 (2005).

[10] (a) S.-Q. Zang, Y. Su, Y. Song, Y.-Z. Li, Z.-P. Ni, H.Z. Zhu, Q.-J. Meng. *Cryst. Growth Des.*, 6, 2369 (2006); (b) S. Zang, Y. Su, Y. Li, Z. Ni, Q. Meng. *Inorg. Chem.*, **45**, 174 (2006); (c) D.R. Whitcomb, M. Rajeswaran. *Polyhedron*, **25**, 1747 (2006); (d) Z. Su, J. Xu, J. Fan, D.-J. Liu, Q. Chu, M.-S. Chen, S.-S. Chen, G.-X. Liu, X.-F. Wang, W.-Y. Sun. *Cryst. Growth Des.*, **9**, 2801 (2009).

[11] (a) G. Che, X. Wang, C. Liu, J. Chen, S. Wang, X. Li. *J. Coord. Chem.*, **65**, 4185 (2012); (b) F. Zhang, X.-T. Huang, Y.-Y. Tian, Y.-X. Gong, X.-Y. Chen, J.-J. Lin, D.-S. Lu, Y.-L. Zhang, R.-H. Zeng, S.-R. Zheng. *J. Coord. Chem.*, **66**, 2659 (2013).

[12] (a) J.G. Young, W.J. Onyebuagu. *J. Org. Chem.*, **55**, 2155 (1990); (b) A.G. Gürek, Ö. Bekâroğlu. *J. Chem. Soc., Dalton Trans.*, 1419 (1994).

[13] (a) Z. Jiang, N.-S. Chen, J.-D. Wang, J.-L. Huang. *Chin. J. Inorg. Chem.*, **21**, 1891 (2005); (b) L. Yang, M.-J. Lin, X.-L. Zhu, X.-Z. Xu, J.-D. Wang. *J. Mol. Catal. A*, **253**, 25 (2006); (c) M.-J. Lin, L. Yang, J.-D. Wang. *J. Mol. Catal. A*, **273**, 157 (2007).

[14] G.M. Sheldrick. *SHELXS-97: Program for Crystal Structure Refinement*, University of Gottingen, Gottingen, Germany (1997).

[15] (a) J. Xu, J. Cheng, W. Su, M. Hong. *Cryst. Growth Des.*, **11**, 2294 (2011); (b) G.-L. Zhuang, X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng. *CrystEngComm*, **12**, 2691 (2010).