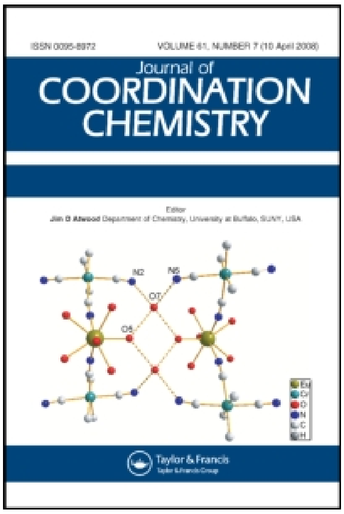

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A 2D lanthanum coordination polymer with π-π stacking

Yanjuan Qi[ab]; Hui Li[a]; Chunming Liu[b]; Changwen Hu[a]
[a] Department of Chemistry, Beijing Institute of Technology, Beijing, P.R. China [b] The Department of Chemistry of Changchun Teachers' College, Changchun, P.R. China

To cite this Article Qi, Yanjuan , Li, Hui , Liu, Chunming and Hu, Changwen(2008) 'A 2D lanthanum coordination polymer with π-π stacking', Journal of Coordination Chemistry, 61: 3, 315 — 321
To link to this Article: DOI: 10.1080/00958970701318434
URL: http://dx.doi.org/10.1080/00958970701318434

Journal of Coordination Chemistry
Vol. 61, No. 3, 10 February 2008, 315–321

A 2D lanthanum coordination polymer with π–π stacking

YANJUAN QI†‡, HUI LI†, CHUNMING LIU‡ and CHANGWEN HU*†

†Department of Chemistry, Beijing Institute of Technology, Beijing 100081, P.R. China
‡The Department of Chemistry of Changchun Teachers' College,
Changchun 130032, P.R. China

(*Received 30 March 2006; in final form 16 August 2006*)

A 2D lanthanum coordination polymer $La_2(1,10\text{-phen})_2(e,a\text{-}cis\text{-}1,4\text{-chdc})_3 \cdot 2.5H_2O$ (chdc = cyclohexanedicarboxylic acid; phen = 1,10-phenanthroline) **1** which contains two-dimensional (2-D) lanthanum-organic sheets, was prepared under hydrothermal conditions and characterized by elemental analyses, IR spectra, TG analysis, and single-crystal X-ray diffraction. In the structure of **1**, the La site is nine-coordinate by two nitrogen atoms from 1,10-phen and seven oxygen atoms from several 1,4-chdc ligands, connected into a 2-D coordination polymer, with the flexible 1,4-chdc spacers. The 2-D layers are extended into a 3-D framework by π–π interactions between adjacent layers.

Keywords: Polymeric; Lanthanum; *e*,*a*-*cis*-conformation; Supramolecular

1. Introduction

The rational design and construction of inorganic–organic hybrid materials by flexible multidentate ligands have received attention due to their novel structures as well as their special properties [1–6]. A guiding principle of our work is the attempt to control conformations of flexible spacer ligands in the architecture of the products. Flexible spacer ligand is the origin of the dynamic functionalizing framework that is a challenge in material science and crystal engineering. 1,4-cyclohexanedicarboxylic acid is a good candidate [7–11] and its limited flexibility may make versatile structures. At the same time, 1,4-cyclohexanedicarboxylic acid possess chair-type structures with *cis*- and *trans*-conformations (scheme 1). By changing pH values, the ratio of *cis* and *trans* chdc ligands in a lanthanide compound can be successfully controlled under hydrothermal condition [12]. Hence, chdc has potential application in the construction of chiral coordination polymers.

Recently, the conformations of 1,4-cyclohexanedicarboxylic acid were separated completely [13]. We previously reported novel single-helix coordination polymers with the d^{10} transition metal ions [14]. Here, the lanthanide complex

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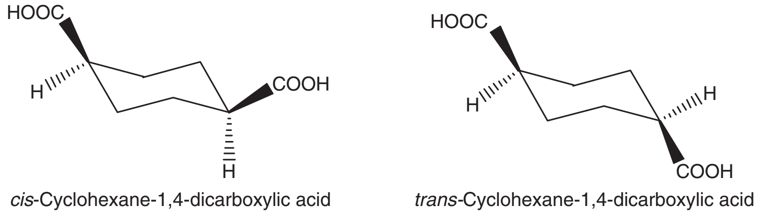
*Corresponding author. Tel.: +86-10-82571381. Email: huchw@nenu.edu.cn
[†] Northeast Normal University.
[‡] Beijing Institute of Technology.

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701318434



Scheme 1. The conformations of 1,4-cyclohexanedicarboxylic acid.

La_2(1,10-phen)$_2$(*e*,*a*-*cis*-1,4-chdc)$_3 \cdot 2.5H_2O$ with a 2-D sheet structure is synthesized under hydrothermal conditions.

2. Experimental

2.1. *General methods*

All reagents were purchased commercially and used without further purification. Deionized water was used for the hydrothermal synthesis. The hydrothermal reaction was performed in a 15 mL Teflon-lined stainless steel autoclave at 190°C under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. La was determined by ICP-AES analysis. The infrared spectra of the compound were obtained on an Alpha Centaurt FT/IR spectrometer with pressed KBr pellets in the 4000–500 cm^{-1} regions. A Perkin–Elmer TGA7 thermogravimetric analyzer was used to obtain TGA curves in N_2 with temperature increasing at a rate of 10°C min^{-1}.

2.2. *Hydrothermal synthesis*

Compound **1** was synthesized from reaction mixture of $LaCl_3 \cdot 6H_2O$ (0.4 mmol), 1,4-chdc acid (mixture of *cis* and *trans* 99%) (0.4 mmol), 1,10-phen (0.4 mmol), H_2O (10 mL) and NaOH aqueous (6 mol L^{-1}) in a 15 mL Teflon-lined autoclave under autogeneous pressure, at 190°C for five days. After the mixture was slowly cooled to room temperature, yellow crystals of **1** were obtained. Calcd for $La_2C_{42}H_{47}N_4O_{14.5}$: La 24.88%, C 45.13%, H 4.21%, N 5.01%, O 20.77%, Found: 24.0%, C 45.07%, H 4.17%, N 4.81%. IR (KBr pellet, ν/cm^{-1}): 1174.72(s), 1223.28(s), 1348.86(s), 1427.06(s), 1496.02(s), 1515.76(s), 1621.26(s), 847.94(w), 862.59(w).

2.3. *X-ray crystallography determination*

A crystal of $0.4 \times 0.4 \times 0.3\,mm^3$ was examined at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) radiation, and the scan mode in the range of $1.71^\circ < \theta < 27.48^\circ$. Cell parameters were obtained by global refinement of the positions of all collected reflections. An empirical absorption correction was applied. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program. All nonhydrogen atoms were refined anisotropically. Crystallographic detail for the structure of **1** is summarized in table 1. Selected bond lengths and angles for **1** are given in table 2.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$La_2C_{42}H_{47}N_4O_{14.5}$
Formula weight	1117.66
Temperature (K)	293(2)
Crystal system	Triclinic
Space group (Å, °)	$P\bar{1}$
a	10.088(2)
b	10.650(2)
c	12.870(3)
α	68.96(3)
β	88.47(3)
γ	67.68(3)
Volume (Å^3)	1184.2(4)
Z	2
Reflections collected	7687
Independent reflections	6610 (R(int) = 0.0505)
Goodnees-of-fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0600$, $wR_2 = 0.1363$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

La(1)–O(3)	2.604(11)	La(1)–O(4)	2.704(15)
La(1)–O(5)	2.532(13)	La(1)–O(7)	2.475(16)
La(1)–O(18)	2.597(15)	La(1)–O(20)	2.611(16)
La(1)–O(31)	2.483(10)	La(1)–N(3)	2.75(2)
La(1)–N(4)	2.761(18)	La(1)–La(2)	4.0736(13)
La(2)–O(1)	2.403(14)	La(2)–O(4)	2.442(13)
La(2)–O(6)	2.518(16)	La(2)–O(10)	2.534(13)
La(2)–O(13)	2.531(17)	La(2)–O(9)	2.554(19)
La(2)–O(31)	2.686(13)	La(2)–N(2)	2.71(2)
O(9)–C(49)	1.21(3)	O(10)–C(49)	1.24(2)
O(18)–C(50)	1.30(3)	O(20)–C(50)	1.30(3)
O(31)–La(1)–O(7)	77.5(5)	O(31)–La(1)–O(5)	73.6(5)
O(7)–La(1)–O(5)	136.0(5)	O(31)–La(1)–O(3)	124.3(4)
O(7)–La(1)–O(3)	79.8(5)	O(5)–La(1)–O(3)	89.9(4)
O(31)–La(1)–O(18)	81.5(5)	O(7)–La(1)–O(18)	74.3(5)
O(5)–La(1)–O(18)	131.4(4)	O(3)–La(1)–O(18)	138.0(4)
O(31)–La(1)–O(20)	82.8(5)	O(7)–La(1)–O(20)	124.6(5)
O(5)–La(1)–O(20)	83.9(5)	O(3)–La(1)–O(20)	149.1(5)
O(18)–La(1)–O(20)	51.7(5)	O(31)–La(1)–O(4)	75.2(4)
O(7)–La(1)–O(4)	68.8(5)	O(5)–La(1)–O(4)	72.1(5)
O(3)–La(1)–O(4)	49.2(4)	O(20)–La(1)–O(4)	151.1(5)
O(18)–La(1)–O(4)	139.7(5)	O(31)–La(1)–N(3)	148.7(5)
O(7)–La(1)–N(3)	81.2(6)	O(5)–La(1)–N(3)	136.4(5)
O(3)–La(1)–N(3)	73.2(5)	O(18)–La(1)–N(3)	70.7(6)
O(20)–La(1)–N(3)	90.8(6)	O(4)–La(1)–N(3)	117.7(6)

3. Results and discussion

3.1. *Description of the crystal structure*

Single crystal X-ray diffraction reveals that **1** features a 3-D supramolecular architecture, containing 2-D lanthanum-organic sheets. In the structure of **1**, the lanthanum-organic complex fragments act as connects in the 2-D coordination polymer, which involves the flexible 1,4-chdc spacers. The 2-D layers are extended into a 3-D framework by π–π interactions between the adjacent layers.

The crystallographically independent La site is nine coordinate by two nitrogen atoms from 1,10-phen and seven oxygen atoms from several 1,4-chdc ligands and can be described as a distorted square monoantiprism. The La–O bond lengths vary from 2.475(16) Å to 2.704(15) Å, and La–N distances are in the range 2.75(2) Å to 2.761(18) Å (figure 1).

There are four bridging carboxyl groups between two La sites. Two display monodentate coordination mode whereas the other two are bidentate (scheme 2). These subunits can be considered as the basic building blocks in constructing the 2-D coordination polymer (figure 2). A view of the polyhedral representation of the 2-D sheet along the *c*-axis is shown in figure 3.

The remaining coordination sites on La are occupied by chelating phen ligands, preventing extension into a third direction. In the structure of **1**, the 1,4-chdc ligand possesses only *e*,*a*-*cis*-conformation, which is the same as Co and Ni complexes [14].

The 2-D layers are extended into a 3-D framework by π–π and hydrogen bonding interactions between the adjacent layers. The separations of the aromatic rings was 3.274 Å indicating strong π–π interactions (figure 4), and typical value for hydrogen bonds observed is 2.892 Å suggesting the existence of significant hydrogen bonding interactions. To the best of our knowledge, it is the first example

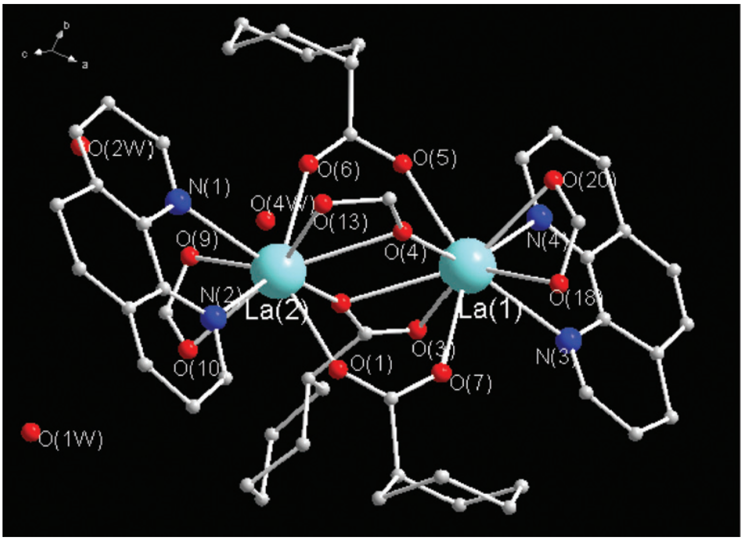
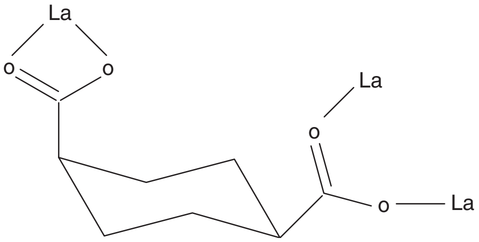


Figure 1. The ORTEP drawing for $La_2(1,10\text{-phen})_2(e,a\text{-}cis\text{-}1,4\text{-chdc})_3 \cdot 2.5H_2O$.



Scheme 2. The coordination mode of 1,4-cyclohexanedicarboxylic acid in compound **1**.

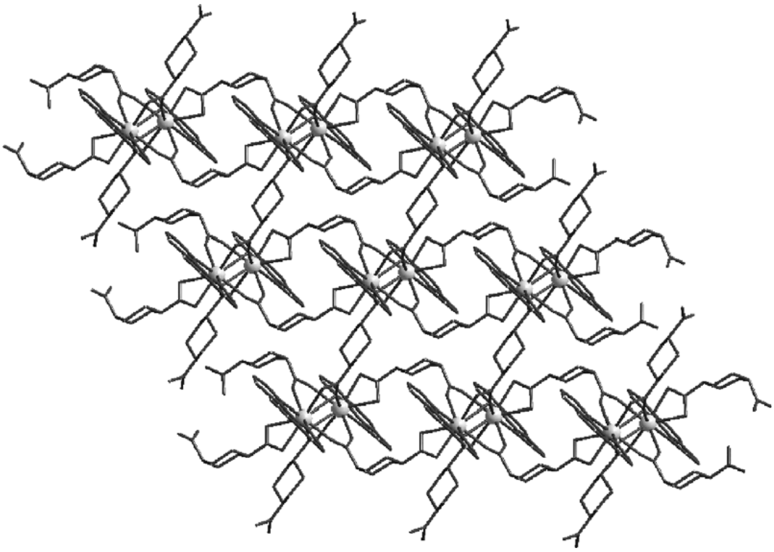


Figure 2. The 2-D layer structure of **1**.

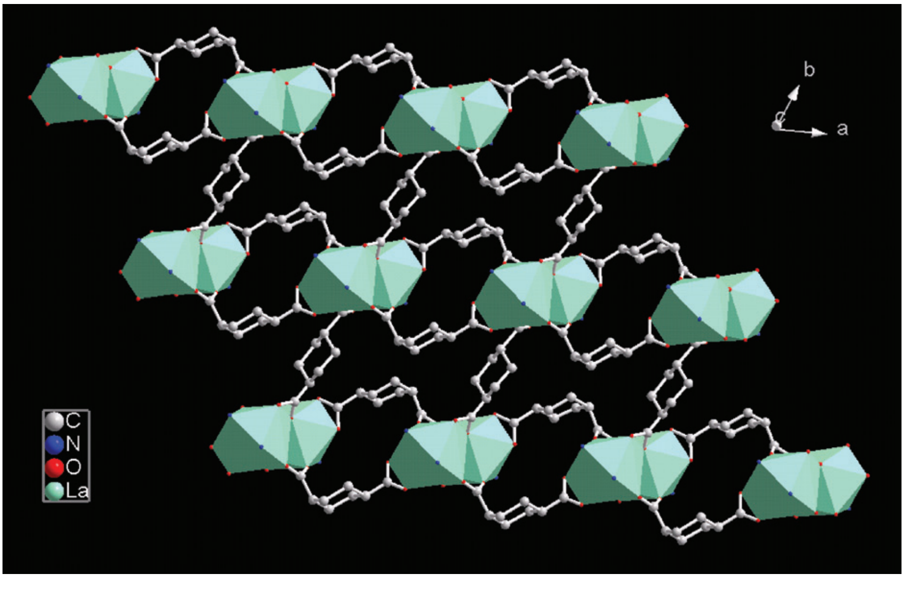


Figure 3. Polyhedral representation of the 2-D sheet of **1**. For the sake of clarity, all hydrogen atoms and the carbon atoms from the phen ligands are omitted.

of the lanthanide coordination polymer combination of 1,4-chdc ligands and chelating ligands.

To check the stability of this polymer, thermogravimetric analysis (TGA) has been recorded from 20 to 175°C. The results reveal that there are two weight losses for compound **1**. The first occurs between 66.39 to 110.99°C, attributed to the loss

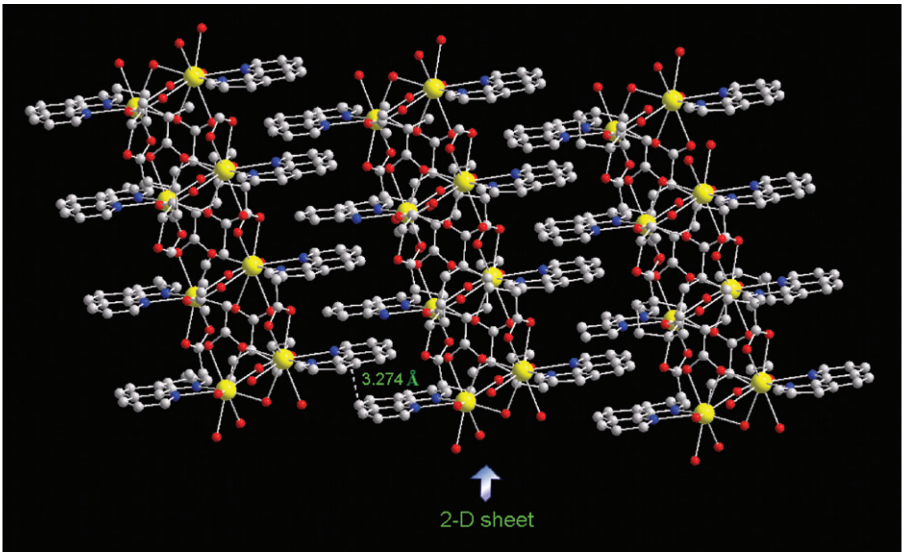


Figure 4. The packing arrangement of the compound, exhibiting the π–π interactions between adjacent layers.

of the crystal water molecules. The observed weight loss (4.75%) is in agreement with the calculated value (4.03%). The weight is almost unchanged in the second stage (196–340°C). Above 340°C, the product begins to lose1,4-chdc and 1,10-phen ligands and then to decompose.

4. Conclusion

A complex containing mixed phen and 1,4-chdc ligands, La_2(1,10-phen)$_2$(*e*,*a*-*cis*-1,4-chdc)$_3 \cdot 2.5H_2O$ (**1**), has been designed and synthesized. It displays a supramolecular structure with "soft" ligands. Design and synthesis of compounds in this system and exploration of their potential properties will be detailed in a forthcoming article.

Supplementary data

The CIF files of **1** have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number: CCDC 252908. X-ray crystallographic files in CIF format for the structure determination of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

The present work was supported by the National Nature Science Foundation of China (20071007 and 20271007) and education office of Jilin province.

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