

镧-酒石酸配合物的银辅助水热合成及晶体结构

王 彦* 刘光祥 陈友存

(安庆师范学院化学化工学院, 安徽省功能配合物重点实验室, 安庆 246011)

摘要: 在反应体系中引入不同的银化合物, 利用水热合成方法制备了 2 个镧-酒石酸配合物 $[\text{La}(\text{TTA})(\text{OA})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**) 和 $[\text{La}_2(\text{TTA})_3(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**2**)。利用元素分析及 X-射线单晶结构测定对其进行了表征。结果表明配合物 **1** 的晶体属于单斜晶系, $P2_1/c$ 空间群; 配合物 **2** 的晶体属于三斜晶系, $P\bar{1}$ 空间群。在配合物 **1** 中, 部分酒石酸被氧化分解成为草酸并作为桥联配体将配合物的层状双(6,3)拓扑结构连接形成三维多孔结构; 化合物 **2** 和 **1** 具有相似的二维结构, 其层状结构单元被不同配位模式的酒石酸配体连接成一个具有三维结构的超分子化合物。

关键词: 晶体结构; 镧配合物; 水热合成

中图分类号: O614.33+1

文献标识码: A

文章编号: 1001-4861(2009)06-1084-07

Hydrothermal Synthesis and Crystal Structures of Two Lanthanum-Tartrate Complexes Cooperated with Ag(I) Complexes

WANG Yan* LIU Guang-Xiang CHEN You-Cun

(School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Functional Coordination Compounds, Anqing Teachers College, Anqing, Anhui 246011)

Abstract: By using hydrothermal method, two lanthanum-tartrate complexes, $[\text{La}(\text{TTA})(\text{OA})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{La}_2(\text{TTA})_3(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**2**), were obtained with cooperation of different Ag(I) complexes. The complexes were characterized by elemental analysis and X-ray crystal structure determination. The crystal structures show that the complex **1** crystallizes in monoclinic, space group $P2_1/c$ with $a=0.610\,71(10)$ nm, $b=0.769\,62(12)$ nm, $c=2.270\,2(3)$ nm, $\beta=91.645(2)^\circ$, $V=1.066\,6(3)$ nm³, $Z=4$, $D_c=2.385$ g·cm⁻³, $F(000)=732$, $\mu=4.058$ cm⁻¹, the final $R=0.048\,5$, $wR=0.103\,5$. While the complex **2** crystallizes in triclinic, space group $P\bar{1}$ with $a=0.613\,08(11)$ nm, $b=0.745\,8(1)$ nm, $c=1.245\,7(2)$ nm, $\alpha=74.662(1)^\circ$, $\beta=88.835(3)^\circ$, $\gamma=89.304(2)^\circ$, $V=0.549\,16(16)$ nm³, $Z=1$, $D_c=2.456$ g·cm⁻³, $F(000)=392$, $\mu=3.951$ cm⁻¹, the final $R=0.052\,0$, $wR=0.088\,7$. In complex **1**, oxidative cleavage was found and the resulted oxalic acid served as bridging-ligand to link the 2D layers of doubled-(6,3) topology to give a porous 3D framework. The complex **2** has similar 2D network with that in **1**, but no cleavage is found. The 2D networks in **2** are further linked into 3D framework by other tartrate ligands with different coordination mode. CCDC: 705232, **1**; 705233, **2**.

Key words: crystal structure; La(III) complex; hydrothermal synthesis

收稿日期: 2008-11-04。收修改稿日期: 2009-03-31。

安徽省教育厅自然科学基金资助项目(No.KJ2008B005), 国家自然科学基金(No.20771006)。

*通讯联系人。E-mail: njwangy@126.com

第一作者: 王 彦, 男, 28 岁, 博士, 讲师; 研究方向: 配位化学。

0 Introduction

In recent years, many chemists and material scientists have paid their attentions to build coordination polymers consisting of inorganic and organic components due to their potential applications in catalysis, magnetism, adsorption and separation materials etc. as well as their fascinating structural diversities^[1,2]. A literature survey shows that the carboxylic ligands have been found to be one of the most useful organic building blocks in construction of MOFs owing to the diversity of the binding modes of carboxylate group to metal atom and many MOFs have been obtained by self-assembly reactions of carboxylate-containing ligands with transition or lanthanide metal salts^[3-7]. In these reports, the majority has been the complexes with carboxylate-containing ligands with aromatic cores, however, the use of carboxylic ligands with flexible carbon-chain spacers are less documented. Meanwhile, chiral coordination complexes are recently attracting intense interest due to their fascinating potential applications in enantioselective separation, asymmetric catalysis, nonlinear optical materials, magnetic materials and guest-host inclusion^[8-12]. The use of chiral molecules as building blocks is a convenient way for the construction of chiral coordination complexes^[13], among which tartaric acid is a simple and readily potential chiral ligand source^[14].

Furthermore, the use of lanthanide salts for synthesizing MOFs is now attracting more and more attentions for their high coordination numbers along with distinguished magnetic and luminescent properties^[15]. Considering the present development of lanthanide structural chemistry, it appears somewhat surprising that the crystal structures of compounds with tartaric acid are rarely reported.

Our research is focused on synthesizing novel coordination polymers from carboxylic ligands. In this paper, we report novel coordination frameworks $[\text{La}(\text{TTA})(\text{OA})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{La}_2(\text{TTA})_3(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**2**) assembled from the tartaric acid (H_2TTA) and corresponding lanthanum salts with cooperation of different Ag(I) complexes under hydrothermal conditions, which may provide useful strategy to construct

new coordination frameworks.

1 Experimental

1.1 General

All commercially available chemicals including tartaric acid are reagent grade and used as received without further purification. C, H and N analyses were made on Elementar Vario EL-III elemental analyzer. Infrared (IR) spectra were recorded on Nicolet AVATAR 360 FTIR spectrophotometer by using KBr discs.

1.2 Synthesis of $[\text{La}(\text{TTA})(\text{OA})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**)

To a suspension of tartaric acid (H_2TTA) (0.037 5 g, 0.25 mmol) in 5 mL water was added La_2O_3 (0.016 3 g, 0.05 mmol), Ag_2O (0.023 7 g, 0.1 mmol) and 10 mL water. After being stirred for 30 min, the resulting solution was sealed into a bomb equipped with a Teflon liner and heated at 180 °C for 48 h. After slow cooling of the reaction mixture to room temperature, colorless column crystals of **1** were obtained in *ca.* 25% yield. Anal. Calcd for compound **1**, $\text{C}_5\text{H}_8\text{La}_1\text{O}_{11}(\%)$: C 15.68, H 2.11; found(%): C 15.75, H 2.30.

1.3 Synthesis of $[\text{La}_2(\text{TTA})_3(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**2**)

To a suspension of tartaric acid (H_2TTA) (0.045 0 g, 0.3 mmol) in 5 mL water was added La_2O_3 (0.032 6 g, 0.1 mmol), AgNO_3 (0.0175 g, 0.1 mmol) and 10 mL water. After being stirred for 30 min, the resulting solution was sealed into a bomb equipped with a Teflon liner and heated at 140 °C for 65 h. After slow cooling of the reaction mixture to room temperature, colorless plate-like crystals of **2** were obtained in *ca.* 40% yield. Anal. Calcd for compound **2**, $\text{C}_{12}\text{H}_{22}\text{La}_2\text{O}_{23}(\%)$: C 17.75, H 2.74; found(%): C 18.02, H 2.41.

1.4 Crystal structure determinations

The data collections for complexes **1**, **2** were made on a Bruker Smart Apex CCD with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 296 and 291 K, respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The hydrogen atoms except for those of water molecules were generated geometrically. All the calculations were performed on a personal computer with the Bruker SHELXTL program package^[16]. Details of the crystal

parameters, data collection, and refinement are summarized in Table 1. Selected bond lengths and bond angles for complex **1** and **2** in Table 2. CCDC: 705232, **1**; 705233, **2**.

Table 1 Crystallographic data for complex **1** and **2**

Compound	1	2
Empirical formula	C ₅ H ₈ LaO ₁₁	C ₁₂ H ₂₂ La ₂ O ₂₃
Formula weight	383.02	812.12
Temperature / K	296(2)	291(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.610 71(10)	0.613 08(11)
<i>b</i> / nm	0.769 62(12)	0.745 8(1)
<i>c</i> / nm	2.270 2(3)	1.245 7(2)
α / (°)		74.662(1)
β / (°)	91.645(2)	88.835(3)
γ / (°)		89.304(2)
<i>V</i> / nm ³	1.066 6(3)	0.549 16(16)
<i>Z</i>	4	1
<i>D_c</i> / (g·cm ⁻³)	2.385	2.456
Absorption coefficient / cm ⁻¹	4.058	3.951
<i>F</i> (000)	732	392
θ range / (°)	2.79~26.00	1.70~26.00
Reflections collected	5 536	5 106
Independent / observed reflections (<i>R_{int}</i>)	2 094 / 1 388 (0.045 2)	4 132 / 3 279 (0.024 4)
Goodness of-fit on <i>F</i> ²	0.993	1.046
<i>R</i> [<i>I</i> >2σ(<i>I</i>)]	0.048 5	0.052 0
<i>wR</i> [<i>I</i> >2σ(<i>I</i>)]	0.103 5 ^a	0.088 7 ^b

^a $w=1/[\sigma^2(F_o^2)+(0.058\ 2P)^2]$ where $P=(F_o^2+2F_c^2)/3$; ^b $w=1/[\sigma^2(F_o^2)+(0.044\ 1P)^2]$ where $P=(F_o^2+2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and bond angles (°) for complex **1** and **2**

1					
La1-O6#1	0.249 0(5)	La1-O5#2	0.250 1(5)	La1-O1	0.251 1(5)
La1-O7	0.254 9(5)	La1-O2	0.256 5(5)	La1-O4#2	0.259 3(5)
La1-O1W	0.258 7(5)	La1-O8#3	0.259 5(5)	La1-O3	0.267 1(5)
O6#1-La1-O5#2	126.74(16)	O6#1-La1-O1	74.62(16)	O5#2-La1-O1	73.41(16)
O6#1-La1-O7	133.85(17)	O5#2-La1-O7	75.93(16)	O1-La1-O7	147.74(17)
O6#1-La1-O2	149.85(17)	O5#2-La1-O2	70.34(16)	O1-La1-O2	90.03(15)
O7-La1-O2	70.23(16)	O6#1-La1-O4#2	69.21(16)	O5#2-La1-O4#2	60.74(15)
O1-La1-O4#2	71.37(16)	O7-La1-O4#2	101.90(16)	O2-La1-O4#2	130.71(15)
O1W-La1-O4#2	144.02(15)	O5#2-La1-O1W	147.59(17)	O1-La1-O1W	126.91(17)
O7-La1-O1W	77.38(17)	O2-La1-O1W	83.55(16)	O6#1-La1-O1W	85.31(18)
O6#1-La1-O8#3	71.99(17)	O5#2-La1-O8#3	106.91(15)	O1-La1-O8#3	137.24(16)
O7-La1-O8#3	62.44(16)	O2-La1-O8#3	131.30(15)	O4#2-La1-O8#3	72.29(14)
O1W-La1-O8#3	75.96(15)	O6#1-La1-O3	75.40(16)	O5#2-La1-O3	121.05(14)
O1-La1-O3	60.80(15)	O7-La1-O3	131.71(16)	O2-La1-O3	74.46(16)
O4#2-La1-O3	126.17(15)	O1W-La1-O3	66.75(15)	O8#4-La1-O3	131.75(14)

Continued Table 2

2					
La1-O6#1	0.245 0(7)	La1-O7	0.245 9(7)	La1-O1	0.254 3(7)
La1-O1W	0.254 6(6)	La1-O5#2	0.255 9(7)	La1-O4#2	0.259 1(7)
La1-O2W	0.261 0(7)	La1-O9	0.266 1(7)	La1-O13	0.269 4(7)
La2-O12#3	0.245 8(6)	La2-O8#4	0.245 8(8)	La2-O2	0.251 5(7)
La2-O11	0.252 5(8)	La2-O10	0.255 2(7)	La2-O4W	0.258 0(7)
La2-O17#5	0.263 2(7)	La2-O3W	0.264 8(7)	La2-O3	0.271 8(7)
O6#1-La1-O7	76.5(2)	O6#1-La1-O1	147.0(2)	O7-La1-O1	84.3(2)
O6#1-La1-O1W	86.7(2)	O7-La1-O1W	126.5(2)	O1-La1-O1W	83.4(2)
O6#1-La1-O5#2	129.8(2)	O7-La1-O5#2	76.1(2)	O1-La1-O5#2	68.8(2)
O1W-La1-O5#2	142.9(2)	O6#1-La1-O4#2	69.6(2)	O7-La1-O4#2	67.8(2)
O1-La1-O4#2	126.9(2)	O1W-La1-O4#2	149.4(2)	O5#2-La1-O4#2	61.3(2)
O6#1-La1-O2W	132.7(2)	O7-La1-O2W	150.3(2)	O1-La1-O2W	71.9(2)
O1W-La1-O2W	69.3(2)	O5#2-La1-O2W	78.8(2)	O4#2-La1-O2W	112.8(2)
O6#1-La1-O9	73.5(2)	O7-La1-O9	59.7(2)	O1-La1-O9	73.7(2)
O1W-La1-O9	66.8(2)	O5#2-La1-O9	123.8(2)	O4#2-La1-O9	120.9(2)
O2W-La1-O9	126.2(2)	O6#1-La1-O13	67.3(2)	O7-La1-O13	131.8(2)
O1-La1-O13	141.6(2)	O1W-La1-O13	83.01(19)	O5#2-La1-O13	103.4(2)
O4#2-La1-O13	70.3(2)	O2W-La1-O13	69.7(2)	O9-La1-O13	131.4(2)
O12#3-La2-O8#4	145.2(2)	O12#3-La2-O2	73.8(3)	O8#4-La2-O2	85.5(3)
O12#3-La2-O11	130.5(2)	O8#4-La2-O11	68.9(2)	O2-La2-O11	77.8(2)
O12#3-La2-O10	69.9(2)	O8#4-La2-O10	129.8(2)	O2-La2-O10	71.7(2)
O11-La2-O10	63.0(2)	O12#3-La2-O4W	89.3(2)	O8#4-La2-O4W	81.6(2)
O2-La2-O4W	127.8(2)	O11-La2-O4W	139.6(2)	O10-La2-O4W	147.2(2)
O12#3-La2-O17#5	70.9(2)	O8#4-La2-O17#5	137.4(2)	O2-La2-O17#5	136.3(2)
O11-La2-O17#5	106.9(2)	O10-La2-O17#5	72.6(2)	O4W-La2-O17#5	76.8(2)
O12#3-La2-O3W	139.1(2)	O8#4-La2-O3W	70.2(2)	O2-La2-O3W	144.8(2)
O11-La2-O3W	70.0(2)	O10-La2-O3W	104.4(2)	O4W-La2-O3W	74.6(2)
O17#5-La2-O3W	68.9(2)	O12#3-La2-O3	71.0(2)	O8#4-La2-O3	74.4(2)
O2-La2-O3	58.8(2)	O11-La2-O3	124.4(2)	O10-La2-O3	123.2(2)
O4W-La2-O3	69.0(2)	O17#5-La2-O3	128.3(2)	O3W-La2-O3	132.0(2)

Symmetry transformation used to generate equivalent atoms: for 1: #1: $-x, y-1/2, -z+3/2$; #2: $-x+1, y-1/2, -z+3/2$; #3: $-x+1, -y, -z+2$; for 2: #1: $x-1, y-1, z$; #2: $x, y-1, z$; #3: $x+1, y, z$; #4: $x, y+1, z$; #5: $x+1, y+1, z-1$.

2 Results and discussion

2.1 Structure description

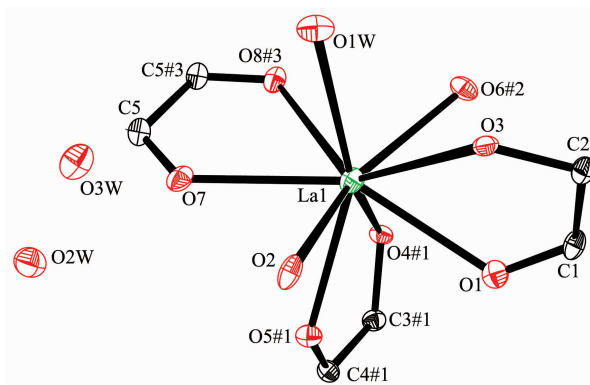
2.2.1 Crystal structure of 1

The crystallographic analysis revealed that the complex **1** crystallized in monoclinic system, space group $P2_1/c$. As shown in Fig.1, the asymmetric unit of complex **1** contains one La(III) ions, one TTA ligand, half OA and two distinct water molecules. In complex **1**, the La (III) ions are nine-coordinated with six carboxyl O

atoms of four distinct tartrate ligands, two carboxyl O atoms of two different carboxylate groups from one OA ligand and one free water molecule. The La-O bond lengths are in the range of 0.249 0(5) to 0.267 1(5) nm, similar to other related La-O distances^[17], and the O-La-O coordination angles vary from 60.74 (15)° to 149.85 (17)°. In complex **1**, all carboxyl groups are deprotonated, in good agreement with IR spectra since no strong band around 1 702 cm⁻¹ for -COOH were found. Each TTA²⁻ acts as μ_4 -bridge linking four lanthanum

atoms (Fig.2a). In complex **1**, the hydroxyl O atoms are in chelating coordination mode with their neighboring carboxylic O atoms and the carboxylate groups of TTA²⁻ ligand are in $\mu_2\text{-}\eta^1\text{:}\eta^1$ mode connecting two metal atoms, which is one of the reported coordination modes of tartrate ligands^[18]. With ignoring the coordination of OA²⁻ ligands, the TTA²⁻ ligands and La(III) atoms form a 2D network of double-layered (6,3) topology with metal-metal distances ranging from 0.610 7(1) to 0.982 5(1) nm (Fig.3a). In complex **1**, oxidative cleavage of some of tartrate ligands were found and resulted in oxalic acids^[19]. The 2D sheets are further linked together by OA²⁻ ligands to give a 3D porous coordination framework with channels dimensions of *ca.* 0.877 nm×0.926 nm (Fig.3b). The uncoordinated water molecules are

trapped into the channels.



Symmetric code: #1: 1-x, -0.5+y, 1.5-z; #2: -x, -0.5+y, 1.5-z, #3: 1-x, -y, 2-z

Fig.1 Asymmetric unit of complex **1**, Thermal ellipsoids are drawn at 30% probability and hydrogen atoms were omitted for clarity

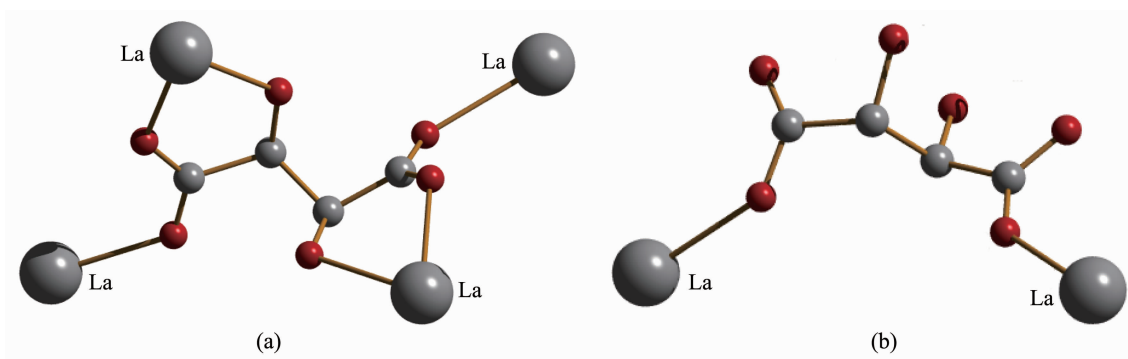


Fig.2 Different coordination modes (a) and (b) of TTA²⁻ ligands found in complexes **1** and **2**, respectively

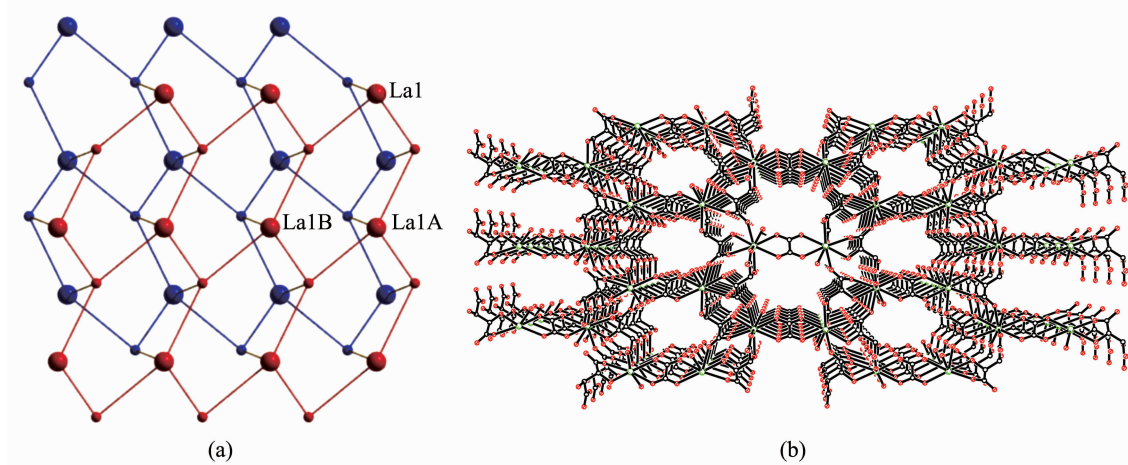


Fig.3 (a) Schematic drawing of the 2D double-layered network of complex **1** viewing along the *c* axis, where the four-connecting TTA²⁻ ligands were represented by four spokes radiation from a solid point and the La(III) atoms by bigger balls; (b) Packing diagram of **1** along the *a* axis, where the guest water molecules were omitted for clarity

2.2.2 Crystal structure of **2**

Complex **2** was also synthesized by hydrothermal method by using AgNO₃ instead of Ag₂O. Complex **2**

crystallizes in triclinic system, space group $P\bar{1}$. The asymmetric unit of **2** is depicted in Fig.4a, which contains two kinds of La (III) atoms with different

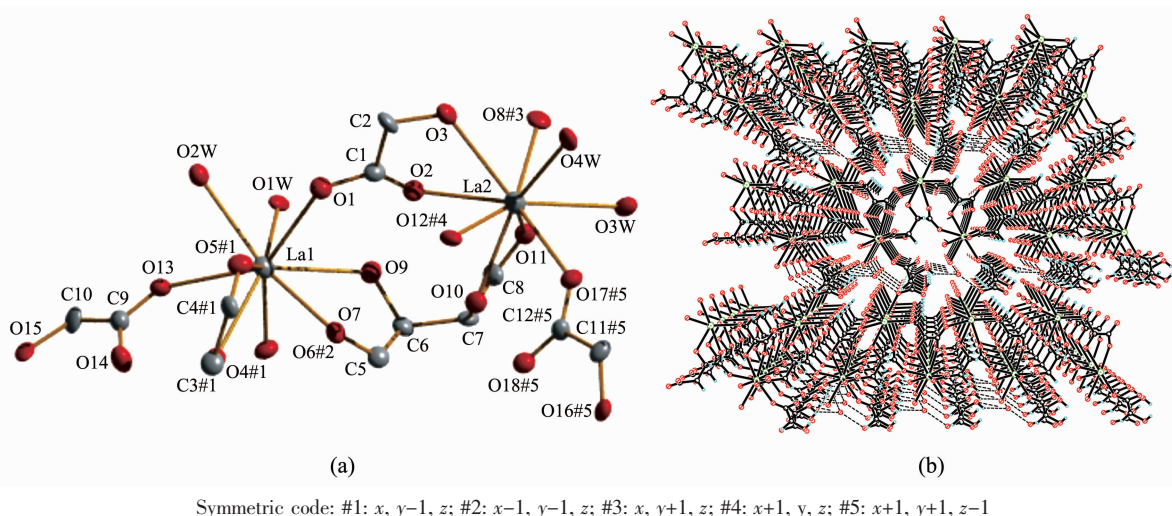


Fig.4 Coordination environment around La(III) atoms in complex **2**, where the thermal ellipsoids were drawn at 30% probability and hydrogen atoms and uncoordinated water molecules were omitted for clarity; (b) 3D framework of complex **2** viewing along the a axis where the hydrogen bonds were indicated by dashed lines

coordination environments. The La1 and La2 atoms are all coordinated with five carboxylic O atoms, two hydroxyl O atoms and two water molecules but with different La-O distances and O-La-O angles. The La-O bond distances are in the range of 0.245 0(7) to 0.271 8(7) nm with the La-O average distance of 0.256 7(7) nm. In complex **2**, the La \cdots La distance of M₂L₂ cycle is 0.617 2(1) nm. There are two kinds of TTA²⁻ ligands of different coordination modes (Fig.2). One acts as the same μ_4 -bridge as that in complex **1** linking four La(III) atoms (e.g. the ligands containing C1, C2, C3, C4 and C5, C6, C7, C8, respectively). The ligand containing C1 links three La1 and one La2 atoms while the ligand containing C5 links three La2 and one La1 atoms. The other TTA²⁻ ligands (e.g. the ligands containing C9, C10, C11 and C12) serves as μ_2 -bridge linking one La1 and one La2 atoms, in which the hydroxyl O atoms do not participate in the coordination and the carboxylate groups adopt μ_1 - η^1 : η^0 coordination mode (Fig.2b). With ignoring the coordination effect of the μ_2 -TTA²⁻ ligand, each La(III) atom connects four ligands and each ligand links four metal atoms to form doubled-(6,3) topological network (Fig.3a) with La \cdots La distances varying from 0.613 1(1) to 0.971 2(1) nm, which is very similar with that in complex **1**. The μ_2 -TTA²⁻ links the 2D layers of **2** together to give a 3D porous coordination framework and the free water

molecules are captured into the channels (Fig.4b). It is interesting that although the Ag(I) complexes were added into the synthetic system, they did not exist in the crystal structures and just served as cooperative materials in the crystallization processes. It is also noteworthy that although the mixed tartaric acid were used in the synthesis, only 2*R*,3*R*- and 2*S*,3*S*-tartrate ligands rather than the meso-one were found in the title complexes. The investigations of other lanthanide-tartrate complexes with/without Ag(I) complex are still in progress.

References:

- [1] Hasegawa S, Horike S, Matsuda R, et al. *J. Am. Soc. Chem.*, **2007**,**129**:2607~2614
- [2] Tzeng B C, Chen B S, Yeh H T, et al. *New J. Chem.*, **2006**,**30**: 1087~1092
- [3] Serre C, Millange F, Thouvenot C, et al. *J. Mater. Chem.*, **2004**, **14**:1540~1543
- [4] Wan Y, Zhang L, Jin L, et al. *Inorg. Chem.*, **2003**,**42**:4985~4994
- [5] Zhang Z H, Shen Z L, Okamura T A, et al. *Cryst. Growth Des.*, **2005**,**5**:191~1197
- [6] HE Yin-Hua(何银华), FENG Xia(封霞), FENG Yun-Long (冯云龙), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(10):1805~1808
- [7] Dalgarno S J, Power N P, Atwood J L. *Coord. Chem. Rev.*, **2008**,**252**:825~841

- [8] Welbes L L, Borovik A S. *Acc. Chem. Res.*, **2005**,**38**:765~774
- [9] Wu C D, Hu A, Zhang L, et al. *J. Am. Chem. Soc.*, **2005**,**127**:8940~8941
- [10] Yu S Y, Zhang Z X, Cheng E C C, et al. *J. Am. Chem. Soc.*, **2005**,**127**:17994~17995
- [11] Wen H R, Wang C F, Song Y, et al. *Inorg. Chem.*, **2005**,**44**:9039~9045
- [12] WANG Guo-Xi(王国喜), LI Bo(李 波), XIONG Ren-Gen(熊仁根), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(11):1994~1996
- [13] Sheng Y W, Wang Y, Okamura T A, et al. *Inorg. Chem. Commun.*, **2007**,**10**:432~436
- [14] Kim Y J, Suh M, Jung D Y. *Inorg. Chem.*, **2004**,**43**:245~250
- [15] Luneau D, Rey P. *Coord. Chem. Rev.*, **2005**,**249**:2591~2611
- [16] Sheldrick G M. *SHELXTL V5.1 Software Reference Manual*, Bruker AXS, Inc., Madison, Wisconsin, USA, **1997**.
- [17] Zhang Z H, Shen Z L, Okamura T A, et al. *Cryst. Growth Des.*, **2005**,**5**:1191~1197
- [18] Yao H G, Ji M, Ji S H, et al. *Inorg. Chem. Commun.*, **2007**,**10**:440~442
- [19] Thuéry P. *Polyhedron*, **2007**,**26**:101~106