

La(III)、Nd(III)与甜菜碱类衍生物形成的包含(H₂O)₆分子簇的配合物的晶体结构

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摘要: 利用配体 1,5-二(3-羧基吡啶基)-N-甲基二乙胺(L)合成 2 种稀土金属配合物 {[La₂L₄(H₂O)₂](ClO₄)₆·6H₂O}_n (**1**)和[Nd₂L₄(DMF)₆(H₂O)₂](ClO₄)₆·4H₂O (**2**)。用红外光谱和 X-射线单晶衍射表征配合物的晶体结构。结构分析表明:配合物 **1** 属于三斜晶系, $P\bar{1}$ 空间群, 其晶胞参数为 $a=1.496\ 6(3)\text{ nm}$, $b=1.559\ 7(4)\text{ nm}$, $c=1.956\ 8(4)\text{ nm}$, $\alpha=86.776(6)^\circ$, $\beta=77.723(7)^\circ$, $\gamma=87.168(7)^\circ$, $Z=2$ 。在配合物 **1** 中, 一对 La(III)原子被 2 个羧基桥联, 形成双核结构; 双核结构进一步被羧基连接, 从而形成平行于 c 轴的一维链。值得注意的是配合物 **1** 的晶体结构中包含着由氢键连接的 6 个 H₂O 分子组成的水分子簇。配合物 **2** 属于三斜晶系, $P\bar{1}$ 空间群, 晶胞参数为 $a=1.040\ 8(4)\text{ nm}$, $b=1.354\ 1(5)\text{ nm}$, $c=2.975(1)\text{ nm}$, $\alpha=94.390(8)^\circ$, $\beta=91.720(7)^\circ$, $\gamma=95.230(4)^\circ$, $Z=2$ 。配合物 **2** 中 4 个羧基连接一对 Nd(III)原子, 形成四轮状结构, 其中 2 个羧基采取 *syn-syn* 双原子桥联模式, 而其余 2 个羧基则采取单原子桥联模式。

关键词: 双齿甜菜碱类衍生物; La(III)配位化合物; Nd(III)配位化合物; (H₂O)₆ 分子簇; 分子夹

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Crystal and Molecular Structures of La(III) and Nd(III) with Bidentate Betaine Derivative 1,5-Bis(3-carboxypyridiniuties)-N-methyl-diethylamine Containing (H₂O)₆ Clusters

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Abstract: Two lanthanide coordination compounds of the bidentate betaine derivative 1,5-bis(3-carboxypyridiniuties)-N-methyl-diethylamine (L), namely, {[La₂L₄(H₂O)₂](ClO₄)₆·6H₂O}_n (**1**) and [Nd₂L₄(DMF)₆(H₂O)₂](ClO₄)₆·4H₂O (**2**) have been prepared and characterized by infrared spectrum (IR) and single crystal X-Ray structure analysis. Both **1** and **2** are crystallized in space group $P\bar{1}$ with $a=1.496\ 6(3)\text{ nm}$, $b=1.559\ 7(4)\text{ nm}$, $c=1.956\ 8(4)\text{ nm}$, $\alpha=86.776(6)^\circ$, $\beta=77.723(7)^\circ$, $\gamma=87.168(7)^\circ$, $Z=2$ for **1**, and $a=1.040\ 8(4)\text{ nm}$, $b=1.354\ 1(5)\text{ nm}$, $c=2.975(1)\text{ nm}$, $\alpha=94.390(8)^\circ$, $\beta=91.720(7)^\circ$, $\gamma=95.230(4)^\circ$, $Z=2$ for **2**, respectively. In **1**, pairs of La(III) atoms are bridged by two carboxylate groups forming a di-metal core structures which are linked by carboxylatos to a coordination string running parallel to the c axis. In addition, a notable feature in **1** is the existence of (H₂O)₆ clusters which consist of cyclic (H₂O)₄ clusters as cores. In **2**, the coordination cation is of a carboxylato-bridged tetrakis-carboxylato wheel like di-metal core structure with a pair of carboxylate groups acting in a *syn-syn* bridging mode and the other acting in chelating/mono atom bridging mode. CCDC: 998597, **1**; 998596, **2**.

Key word: bidentate betaine derivative; La(III) coordination compound; Nd(III) coordination compound; (H₂O)₆ cluster; molecular clip

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0 Introduction

Carboxylic acids, which show various coordination modes towards metal ions owing to the special geometry and electronic structure of carboxylate group, are undoubtedly one set of the most important organic building blocks in coordination chemistry^[1-3]. Numerous crystal structures of metal carboxylates have been reported, and among them the coordination compounds of carboxylic acids with lanthanide ions are of great interests because of the high and readily changeable coordination numbers and coordination geometry of lanthanide ions, which enable the resulting coordination compounds exhibit diverse topological structures^[4].

In our previous study, a bidentate betaine derivative 1,5-bis (4-carboxypyridinium)-*N*-methyl-diethylamine was adopted as an organic building block in preparing Cd(II) coordination compounds, and it is found that a pair of the ligand molecules, both take a “U-shape” conformation, coordinate to different Cd(II) ions forming a 36-membered coordination ring^[5]. The formation of large coordination ring may be attributed to the parallel orientation of the carboxylate group to the N⁺-C bond. In present study, a similar bidentate betaine derivative 1,5-bis(3-carboxypyridinium)-*N*-methyl-diethylamine in which the angle between the carboxylate group and N⁺-C bond is 120° was allowed to react with different lanthanide salts to inspect if the different orientation of the carboxylate group could enable both carboxylate groups of the molecule coordinate to the same metal ion, and thus the molecule acts as a molecular clip.

1 Experimental

1.1 Synthesis

1.1.1 Synthesis of 1,5-bis(3-carboxypyridinium)-*N*-methyl-diethylamine (L)

To the solution of *N*-methyl-*N*-bis(2-bromoethyl) amine hydrobromide^[6] (13.03 g, 0.04 mol) in ethanol (60 cm³) ethyl nicotinate (13.30 g, 0.088 mol, excess 10%) was added. The mixture was refluxed for *c.a.* 36 h and the resulting precipitate was filtered, rinsed

with acetone for several times and air-dried. The product was dissolved in HCl (15%, 60 cm³) and refluxed for 5 h. After removal of the solvent under reduced pressure, the residue was dissolved in minimum amount of water and treated with 1,2-epoxypropane at *c.a.* 30 °C until pH ≈ 7. Remove the solvent under reduced pressure, dissolve the syrupy residual in DMF, and vigorously stir the mixture until the precipitate formed. The raw product was recrystallized in H₂O/DMF. Yield: 68%. ¹H NMR (400 MHz, D₂O) δ 2.39 (s, 3H, N-CH₃), 2.99~3.02 (t, *J*=4 Hz, 8 Hz, 4H, CH₂-N-CH₂), 4.57~4.59(t, *J*=4 Hz, 4H, N-CH₂), 8.07~8.08 (d, *J*=4 Hz, 4H, CH=N), 8.65~8.65 (d, *J*=4 Hz, 4H, OOC=CH). Anal. Calcd. For C₁₇H₁₉N₃O₄·3H₂O (%) C, 53.26; H, 6.57; N, 10.96. Anal. Found. (%) C, 53.10; H, 6.52; N, 10.86. IR: 1640 cm⁻¹ (carboxylate ν_{asym}), 1 360 cm⁻¹ (carboxylate ν_{sym}).

1.1.2 Synthesis of {[La₂L₄(H₂O)₂](ClO₄)₆·6H₂O}_n (**1**)

To mixed EtOH/H₂O (1:2, *V:V*, 8 cm³) solvent L (183 mg, 0.5 mmol) and La(ClO₄)₃·6H₂O (445 mg, 1.0 mmol) were added, and the resulting solution was heated under stirring at *c.a.* 60 °C for 15 min, cooled to room temperature and filtered. Colorless prismatic crystals of **1** suitable for single crystal X-Ray structure analysis were obtained after standing the filtration at ambient temperature for several days. IR (cm⁻¹): 1 642, 1 410, 1 208, 1 093, 683.

1.1.3 Synthesis of [Nd₂L₄(DMF)₆(H₂O)₂]₂(ClO₄)₆·4H₂O (**2**)

The preparation procedure of this compound was analogous to that for **1**, with L (192 mg, 0.5 mmol) and Nd(ClO₄)₃·6H₂O (275 mg, 0.5 mmol). However, an oily residual was formed after the vaporization of the solvent. Pale purple prismatic crystals of **2** suitable for single crystal X-Ray structure analysis were obtained by carrying out the reaction in mixed DMF/H₂O solvent. IR (cm⁻¹): 1 646, 1 414, 1 214, 1 084, 680, 626.

1.2 X-ray diffraction data collection, structure determination and refinement

Information concerning X-ray data collection and structure refinement is summarized in Table 1. The intensities for both **1** and **2** were collected at 293(2) K

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

	1	2
Formula	C ₆₈ H ₉₂ Cl ₆ La ₂ N ₁₂ O ₄₈	C ₅₂ H ₉₂ Cl ₆ N ₁₂ Nd ₂
Formula weight	2 336.06	2 090.56
Crystal system	Triclinic	Triclinic
λ / nm	0.071 073	0.071 073
Space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
Crystal size / mm	0.20×0.18×0.21	0.15×0.22×0.17
a / nm	1.496 6(3)	1.040 8(4)
b / nm	1.559 7(4)	1.354 1(6)
c / nm	1.956 8(4)	2.975(1)
α / (°)	86.776(6)	94.390(8)
β / (°)	77.723(7)	91.720(7)
γ / (°)	87.168(7)	95.230(4)
V / nm ³	4.455(2)	4.160(3)
Z	2	2
D_c / (g·cm ⁻³)	1.742	1.669
$F(000)$	2 368	2 124
μ / cm ⁻¹	12.35	15.28
θ range / (°)	1.07 to 27.92	1.61 to 27.88
Reflections collected	41 531	39 161
Independent reflections	20 943 (R_{int} =0.064 2)	19 236 (R_{int} =0.029 7)
Final R indices ($I > 2\sigma(I)$)	0.063 5	0.050 7
wR	0.162 7	0.140 1
Goodness of fit on F^2	1.056	1.009
Data / restraints / parameters	20 943 / 63 / 1 256	19 236 / 151 / 1 135

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$; **1**: $a=0.068$ 5, $b=7.821$; **2**: $a=0.100$ 7, $b=1.270$ 1.

on a Bruker SMART Apex II diffractometer (graphite-monochromated Mo $K\alpha$ radiation: $\lambda=0.071$ 073 nm, ω -scan). Adsorption correction based on multi-scan was applied to the intensity data processing.

Both structures of **1** and **2** were solved by the direct method using SIR2011 software^[7], and the non-hydrogen atoms were refined anisotropically by full-matrix least squares method based on all the diffraction data using the SHELXTL 2013 program package^[8]. All hydrogen atoms unless those on coordination free water molecules were placed at their calculated positions, however, the hydrogen atoms on water molecules were located by calculation using Wingx^[9], and allowed to ride on their respective parent atoms and included in the structure factor calculations. In both **1** and **2** there exist some higher

residue peaks (the largest: 2.43×10^3 , 4.69×10^3 e·nm⁻³) which appear near the perchlorate anions and coordination free water molecules in **1** and near the Nd(III) atoms in **2**, show no obvious chemical significance. In both **1** and **2**, one of the perchlorate anions displays some disorder and was handled by splitting the disordered oxygen atoms. In **2**, one of the DMF molecules adopts two orientations about the O-Nd bond with the occupation of 0.72 and 0.28.

Final atomic coordinates and equivalent isotropic thermal parameters along with their estimated standard deviation, a listing of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates as supplementary material are available on request.

CCDC: 998597, **1**; 998596, **2**.

2 Results and discussion

The IR spectra of **1** and **2** were measured using a Bio-Rad FTS 3000 IR spectrometer. The absorptions at 1 640, 1 642 and 1 646 cm^{-1} are assigned to the asymmetric stretching vibration of carboxylate group in **1** and **2**, respectively, and the absorptions at 1 378, 1 410 and 1 414 cm^{-1} for the symmetric stretching vibration. The differences of asymmetric and symmetric stretching vibration absorptions of carboxylate group, $\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$ in **1** and **2** are 280, 233 and 233 cm^{-1} , respectively. The $\Delta\nu$ value is usually used correlating to the coordination mode of carboxylate group in metal carboxylates. The approximately same $\Delta\nu$ values in both **1** and **2** are significantly less than that in **L**, indicating a chelating coordination mode existing in **1** and **2**^[10].

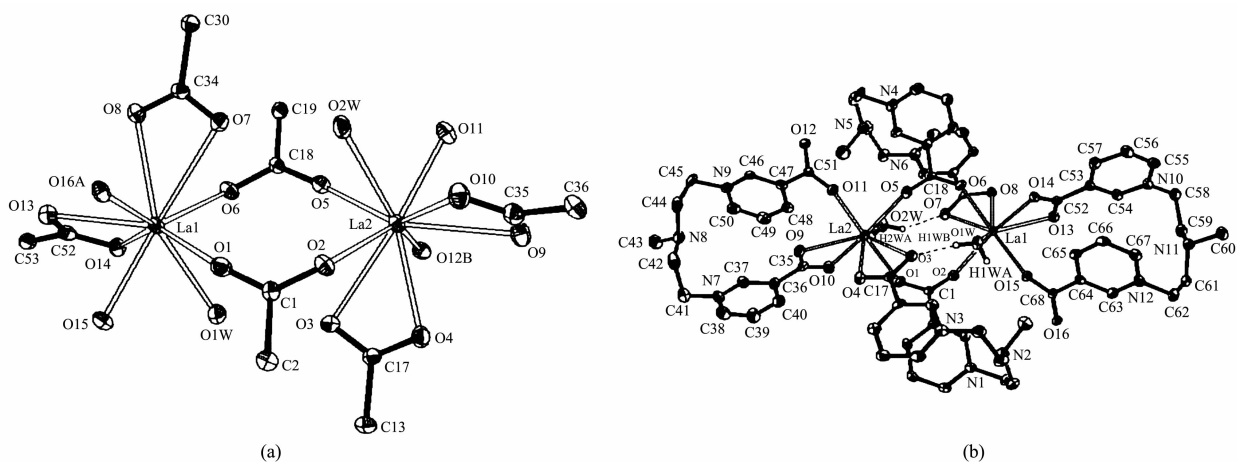
2.1 Crystal structure of **1**

As depicted in Fig.1, the asymmetric unit contains a $[\text{La}_2\text{L}_4(\text{H}_2\text{O})_2]$ motif, which consists of a pair of carboxylato-bridged La(III) atoms. Both La(III) atoms are in a MO_9 coordination sphere, and are nearly related by an inverse center. Of the nine ligating oxygen atoms, four come from a pair of chelating carboxylate groups, four from bridging carboxylate groups and one from an aqua ligand. The M-O bond lengths and bond angles are listed in Table 2.

The di-metal core structure of the motif is

accomplished by a pair of carboxylate groups of different **L** molecules bridging two La(III) atoms with a separation of 0.537 54(9) nm. Both La(III) atoms are located on the same side of the bridging-carboxylate groups and are 0.088 6(8), 0.146 9(8) nm (La1, La2 to O1/O2/C1/C2) and 0.058 8 (8), 0.148 9 (7) nm (La1, La2 to O5/O6/C18/C19) away from the planes. Each of the four **L** molecules adopts a similar “U-shape” conformation with one of its carboxylate groups chelating to and another ligating to the same La(III) atom, thus forming a 16-membered coordination ring. The motif is planar with its four **L** molecules arranged nearly perpendicular mutually. The adjacent motifs are linked by bridging carboxylate groups with separations of 0.589 9(1) and 0.602 3(1) nm, respectively, to a positive charged string which runs parallel to the *c* axis (Fig.2).

Although there are six coordination free water molecules in the asymmetric unit, they have no obvious hydrogen bonding interactions with the aqua ligands and oxygen atoms of carboxylate groups on the coordination strings. However, a plenty of hydrogen bonds exist between the water molecules, water molecules and perchlorate anions. Among the hydrogen bonded species, the most notable feature is the existence of hydrogen bonded $(\text{H}_2\text{O})_6$ clusters with rhombic $(\text{H}_2\text{O})_4$ cluster cores (Fig.3). In the $(\text{H}_2\text{O})_4$ core a pair of opposite located water molecules act as



Hydrogen atoms except those on water molecular are omitted for clarity; Thermal ellipsoids are drawn at 45% probability level;

Symmetry code: A: $-x, -y+3, -z+1$; B: $-x, -y+3, -z$

Fig.1 (a) Coordination environment of La(III) in $\{[\text{La}_2\text{L}_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}\}_n$; (b) Molecule structure of $\{[\text{La}_2\text{L}_4(\text{H}_2\text{O})_2](\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}\}_n$

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

1					
La(1)-O(16)A	0.243 3(3)	La(1)-O(6)	0.244 0(3)	La(1)-O(15)	0.245 0(3)
La(1)-O(2)	0.246 0(4)	La(1)-O(14)	0.254 7(3)	La(1)-O(8)	0.257 0(3)
La(1)-O(1W)	0.261 7(4)	La(1)-O(13)	0.266 2(3)	La(1)-O(7)	0.282 8(3)
La(2)-O(5)	0.245 0(4)	La(2)-O(12)B	0.245 7(3)	La(2)-O(11)	0.245 9(3)
La(2)-O(1)	0.249 7(3)	La(2)-O(10)	0.251 1(4)	La(2)-O(4)	0.253 4(4)
La(2)-O(2W)	0.259 3(4)	La(2)-O(9)	0.271 6(4)	La(2)-O(3)	0.280 7(3)
O(8)-La(1)-O(7)	48.2(1)	O(6)-La(1)-O(2)	101.2(1)	O(14)-La(1)-O(13)	50.3(1)
O(4)-La(2)-O(3)	48.5(1)	O(5)-La(2)-O(1)	97.5(1)	O(10)-La(2)-O(9)	50.1(1)
O(1)-C(1)-O(2)	126.784(9)	O(5)-C(18)-O(6)	125.410(9)	O(13)-C(52)-O(14)	123.958(9)
O(7)-C(34)-O(8)	123.794(6)	O(3)-C(17)-O(4)	124.068(6)	O(10)-C(35)-O(9)	124.340(9)
2					
Nd(1)-O(7)	0.239 8(3)	Nd(1)-O(6)	0.243 2(3)	Nd(1)-O(3)	0.243 6(3)
Nd(1)-O(1)A	0.246 3(3)	Nd(1)-O(1W)	0.247 4(3)	Nd(1)-O(4)A	0.248 0(3)
Nd(1)-O(5)	0.249 0(3)	Nd(1)-O(2)	0.253 0(3)	Nd(1)-O(1)	0.275 7(3)
Nd(2)-O(13)	0.242 4(3)	Nd(2)-O(14)	0.242 9(3)	Nd(2)-O(8)	0.251 6(3)
Nd(2)-O(12)	0.247 2(3)	Nd(2)-O(9)B	0.244 6(3)	Nd(2)-O(10)	0.244 0(3)
Nd(2)-O(2W)	0.247 5(3)	Nd(2)-O(11)B	0.248 0(3)	Nd(2)-O(9)	0.281 1(3)
O(1)-Nd(2)-O(2)	49.051(9)	O(1)-C(1)-O(2)	121.980(8)	Nd(1)-O(1)-Nd(1)	105.95(3)
O(3)-C(17)-O(4)	127.00(2)	O(8)-Nd(2)-O(9)	48.476(8)	O(8)-C(27)-O(9)	123.710(7)
O(10)-C(34)-O(11)	127.22(2)	Nd(2)-O(9)-Nd(2)	106.24(3)		

Symmetry codes for 1: A: $-x, -y+3, -z+1$; B: $-x, -y+3, -z$; for 2: A: $-x+1, -y, -z+1$; B: $-x+2, -y+1, -z$.

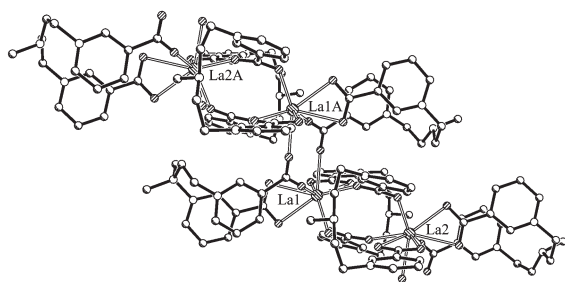


Fig.2 Positive charged string of compound $\{[La_2L_4(H_2O)_2](ClO_4)_6 \cdot 6H_2O\}_n$

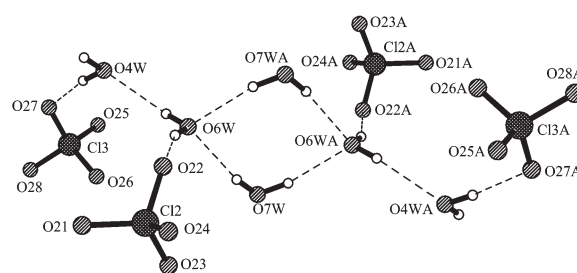


Fig.3 Hydrogen bonded (H₂O)₆ clusters in compound $\{[La_2L_4(H_2O)_2](ClO_4)_6 \cdot 6H_2O\}_n$

hydrogen bond donor and another pair act as hydrogen bond acceptor with O \cdots O distances of 0.278 5(6) and 0.275 6(6) nm, O \cdots O \cdots O angles of 99.2(2)° and 80.8(2)°.

2.2 Crystal structure of compound 2

Reaction of Nd(ClO₄)₃·6H₂O and L in a mixed EtOH/H₂O solvent in the same condition with that in preparing compound 1 did not give a solid precipitate product, instead, after evaporation of the solvent an oily residual was resulted. Single crystals suitable for

single crystal X-ray diffraction structure analysis of compound 2 was obtained by carrying out the reaction in a mixed DMF/H₂O solvent.

Compound 2 crystallizes in space group $P\bar{1}$ (No. 2). The asymmetric unit consists of two chemically identical discrete $[Nd_2L_4(DMF)_6(H_2O)_2]_2(ClO_4)_6 \cdot 4H_2O$ cations, which are differently orientated. As shown in Fig.4, the cation is crystallographically central symmetrical, and is built of two Nd(III) atoms bridged by a pair of carboxylate groups and two μ_2 -oxygen

Table 3 Bond length and bond angle of hydrogen bond in complex **1** and **2**

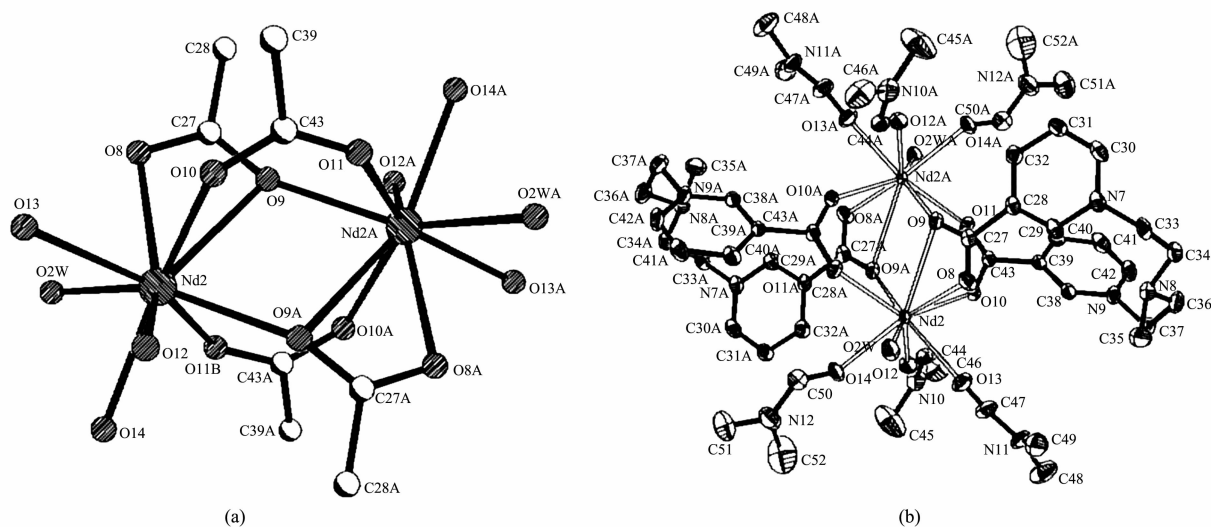
D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠ DHA / (°)
1				
O(1W)-H(1B)-O(3)	0.085	0.185	0.268 6(5)	168.7
O(2W)-H(2WA)-O(37)	0.085	0.230	0.288 4(5)	126.2
O(2W)-H(2WB)-O(7)	0.085	0.195	0.271 0(5)	148.4
O(3W)-H(3WA)-O(40) ^a	0.085	0.191	0.273 3(9)	163.1
O(3W)-H(3WA)-O(39') ^a	0.085	0.216	0.295(1)	154.0
O(3W)-H(3WB)-O(34)	0.085	0.203	0.285 6(7)	162.1
O(4W)-H(4WA)-O(27)	0.085	0.213	0.2967 (6)	166.6
O(5W)-H(5WA)-O(18) ^b	0.085	0.220	0.296 6(9)	149.7
O(6W)-H(6WA)-O(22)	0.085	0.198	0.280 6(6)	164.5
O(6W)-H(6WB)-O(4W)	0.085	0.208	0.288 9(6)	158.8
O(7W)-H(7WA)-O(6W)	0.085	0.195	0.278 5(6)	167.7
O(7W)-H(7WB)-O(6W) ^c	0.085	0.194	0.275 6(6)	160.5
O(8W)-H(8WA)-O(5W) ^b	0.085	0.243	0.322(1)	154.1
O(8W)-H(8WB)-O(32)	0.085	0.194	0.278 4(9)	173.9
2				
O(1W)-H(1WA)-O(5W)	0.085	0.195	0.269 3(7)	145.9
O(1W)-H(1WB)-O(2)	0.085	0.237	0.282 6(4)	114.0
O(1W)-H(1WB)-O(3W)	0.085	0.203	0.276 4(5)	143.6
O(2W)-H(2WA)-O(4W)	0.085	0.194	0.275 2(5)	160.1
O(2W)-H(2WB)-O(6W)	0.085	0.194	0.274 5(5)	158.8
O(5W)-H(5WA)-O(36')	0.085	0.231	0.286(1)	123.2
O(5W)-H(5WB)-O(35) ^a	0.085	0.206	0.272(2)	134.2
O(5W)-H(5WB)-O(42') ^a	0.085	0.239	0.324(2)	177.1
O(4W)-H(4WA)-O(16) ^b	0.085	0.208	0.293 3(6)	179.2
O(4W)-H(4WB)-O(22) ^d	0.085	0.207	0.292 4(5)	179.7
O(6W)-H(6WA)-O(18) ^b	0.085	0.214	0.286 5(8)	142.4
O(6W)-H(6WB)-O(17) ^c	0.085	0.196	0.281 2(7)	179.6
O(3W)-H(3WA)-O(33) ^a	0.085	0.204	0.288 8(5)	179.7
O(3W)-H(3WB)-O(36) ^a	0.085	0.202	0.287(1)	178.6
O(3W)-H(3WB)-O(37') ^a	0.085	0.211	0.278(1)	135.7

Symmetry codes for **1**: ^a $x+1, y, z$; ^b $-x, -y+4, -z$; ^c $-x-1, -y+2, -z+1$; for **2**: ^a $-x+2, -y+1, -z+1$; ^b $-x+1, -y+1, -z$; ^c $-x+2, -y+1, -z$; ^d $x+1, y, z$.

atoms from the other carboxylate groups, and thus has a tetrakis-carboxylato bridged wheel like di-metal core structure. The other coordination positions of each Nd(III) atom are occupied by oxygen atoms from three DMF molecules and one aqua ligand, thus fulfilling the MO₉ coordination sphere of each Nd(III) atoms. In addition, owing to the one-atom bridging, the separation of two Nd(III) atoms (0.421 1(2) nm) are much shorter than the La(III)···La(III) separations found in **1**. Similar to that in **1**, L molecules in **2** also adopt a

“U-shape” conformation, but one of its carboxylate groups acts in a skew syn-syn bridging mode (the M-O-C angles of 141.65(1)° and 132.69(2)°; the distances of Nd(III) atom to the plane of carboxylate group of 0.102 70(4) and 0.039 41(2) nm), and the other one in a chelating/one atom bridging mode.

The chelating/one atom bridging mode is common in the coordination compounds of carboxylic acids. Although theoretical and experimental studies have indicated that the *syn* lone pairs of carboxylate group



Hydrogen atoms except those on water molecular are omitted for clarity; Thermal ellipsoids are drawn at 45% probability level; Symmetry code: A: $-x+2, -y+1, -z$

Fig.4 (a) Coordination environment of $[\text{Nd}_2\text{L}_4(\text{DMF})_6(\text{H}_2\text{O})_2](\text{ClO}_4)_6 \cdot 4\text{H}_2\text{O}$; (b) Molecule structure of $[\text{Nd}_2\text{L}_4(\text{DMF})_6(\text{H}_2\text{O})_2](\text{ClO}_4)_6 \cdot 4\text{H}_2\text{O}$

Table 4 Ln-O bond lengths (nm) in carboxylate exhibiting the combined monoatomic bridging and bidentate chelating mode

Compound	d_1	d_2	d_3	ref
$\text{C}_{48}\text{H}_{40}\text{O}_{32}\text{La}_4$	0.257 1	0.292 3	0.247 5	13
$\text{C}_{42}\text{H}_{38}\text{O}_{22}\text{Cl}_2\text{Ce}_2$	0.257 4	0.275 6	0.246 0	14
$\text{C}_{48}\text{H}_{40}\text{O}_{32}\text{Pr}_4$	0.252 6	0.292 3	0.243 0	15
$\text{C}_{52}\text{H}_{52}\text{N}_{12}\text{O}_{44}\text{Cl}_6\text{Nd}_4$	0.251 7	0.281 1	0.244 6	Compound 2 in this work
$\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_{16.5}\text{Sm}_2$	0.252 0	0.259 7	0.2489	16

are more basic than the anti lone pairs^[11], and therefore the relation $d_3 > d_2$ is expected (d is the distance of Ln and O), studies concerning this mode of transition metal coordination compounds did not show any obvious relationship between d_1 , d_2 and d_3 values^[12]. However, in the case of early rare earth metal coordination compounds d_1 , d_2 and d_3 values indeed exhibit some tendency of $d_2 > d_1 > d_3$ (table 4). These results suggest that the M-O bond lengths d_1 , d_2 and d_3 are mainly determined by the radius of metal ion and coordina-

tion geometrical factors rather than the electronic properties of the lone pairs of the carboxylate group.

3 Conclusion

In 1,5-bis(4-carboxypyridinium)-*N*-methyl-diethylamine the orientation of carboxylate group is parallel to that of the N⁺-C bonds, and the separation between two carboxylate groups of the molecule is large even though the molecule adopts a “U” conformation (Fig.5). Thus, when the molecule interact with metal ions the

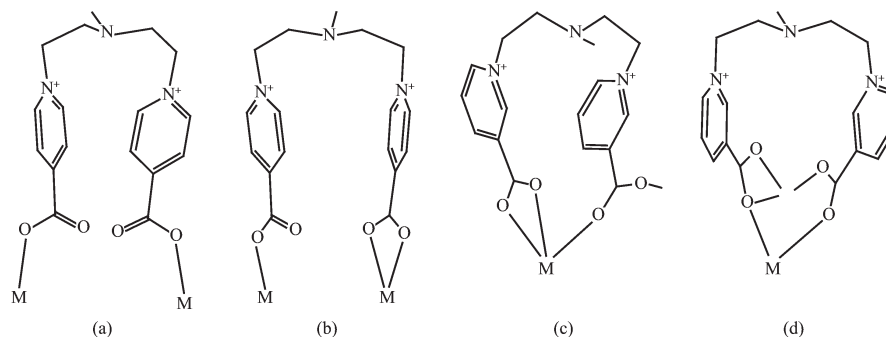


Fig.5 “U-shape” conformation

carboxylate groups ligate to different ones forming large coordination ring. However, in 1,5-bis(3-carboxypyridinium)-*N*-methyl-diethylamine the carboxylate groups are 120° point away from the N⁺-C bonds, and this orientation of the carboxylate groups enable both of them ligate to the same metal ion when the molecule takes a “U” conformation. In this case the molecule acts as a molecular clip with some flexibility.

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