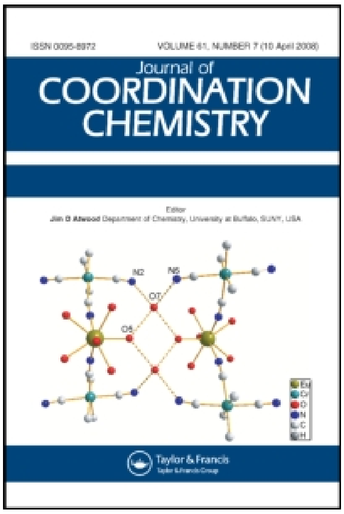

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From polymeric chain compounds to dinuclear complexes via ligand hindrance: the synthesis and structures of lanthanide complexes of N-tolylsulfonyl amino acids

Manbo Zhang[a]; Ruixiang Hu[a]; Fupei Liang[a]; Zhongyuan Zhou[b]
[a] College of Chemistry and Chemical Engineering, Guangxi Normal University, 541004 Guilin, P.R. China [b] Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, P.R. China

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From polymeric chain compounds to dinuclear complexes via ligand hindrance: the synthesis and structures of lanthanide complexes of N-tolylsulfonyl amino acids

MANBO ZHANG†, RUIXIANG HU†,
FUPEI LIANG*† and ZHONGYUAN ZHOU‡

†College of Chemistry and Chemical Engineering,
Guangxi Normal University, 541004 Guilin, P.R. China
‡Department of Applied Biology and Chemical Technology,
The Hong Kong Polytechnic University, Hong Kong, P.R. China

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One-dimensional lanthanide coordination polymers with the formula $[La_2L_6(H_2O)_4]_n$ (L = N-*p*-tolylsulfonylalanate, **1**) and dinuclear ternary complexes with the formula $[LnL_3(bipy)(H_2O)]_2$ (Ln = Gd, Er, L = N-*p*-tolylsulfonylalanate, **2a**–**b**; Ln = Er, Yb, L = N-*p*-tolylsulfonylglycinate, **3a**–**b**) were synthesized. X-ray analysis reveals that compound **1** adopts a chain structure with alternating linkage of two and four bridging TsAla ligands between adjacent La(III) centers, while compounds **2a**–**b** and **3a**–**b** are dinuclear. Crystal data for **1**: triclinic, $P\bar{1}$, $a = 12.8689(18)$, $b = 17.062(2)$, $c = 18.273(2)$ Å, $\alpha = 89.114(3)$, $\beta = 74.763(3)$, $\gamma = 83.617(3)^\circ$, $V = 3846.7(9)$ Å^3, $Z = 2$; for **2a**: monoclinic, $P2_1/n$, $a = 12.586(3)$ Å, $b = 18.397(4)$ Å, $c = 19.526(4)$ Å, $\beta = 97.367(5)^\circ$, $V = 4483.8(18)$ Å^3, $Z = 2$; for **2b**: monoclinic, $P2_1/n$, $a = 12.5122(16)$, $b = 18.374(2)$, $c = 19.531(3)$ Å, $\beta = 97.156(2)^\circ$, $V = 4455.2(10)$ Å^3, $Z = 2$; for **3a**: monoclinic, $P2_1/n$, $a = 12.2578(15)$, $b = 19.037(3)$, $c = 17.952(2)$ Å, $\beta = 92.371(3)^\circ$, $V = 4185.5(9)$ Å^3, $Z = 2$; for **3b**: monoclinic, $P2_1/n$, $a = 12.2312(17)$, $b = 19.007(3)$, $c = 17.960(3)$ Å, $\beta = 92.318(2)^\circ$, $V = 4172.0(10)$ Å^3, $Z = 2$.

Keywords: Lanthanides; N-protected amino acids; 2,2′-bipyridine; Crystal structure

1. Introduction

N-sulfonyl amino acids derived from substitution of an Ar–SO– group on the amine nitrogen of amino acids, have analogous structures to the O-terminal of peptides [1, 2]. Its coordination behaviour may show similar properties to the O-terminal of peptides and proteins. In comparison with corresponding amino acids, N-sulfonyl amino acids possess three types of potential donors – oxygen and nitrogen atoms

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*Corresponding author. Email: fliangoffice@yahoo.com

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from carboxyl, sulfonyl and amine groups, respectively, which may result in different coordination modes [3–6]. Compounds of transition metal-N-sulfonyl amino acids have been investigated widely in the past decades and the research indicates that the coordination modes of N-sulfonyl amino acids are metal- and pH-dependent. At pH = 2–5, the deprotonated carboxylate oxygen is the only binding site [7–10]; at pH = 5–9, the deprotonated amine nitrogen together with carboxylate gives a bidentate chelating mode [11–13]. However, the lanthanide–N-sulfonyl amino acid system has been undeveloped [14]. Lanthanides may exhibit distinct coordination modes different from transition metals. In addition, the unique fluorescence of lanthanides can be used as spectral probes in investigations of biological systems. Following studies of binary complexes of lanthanide and N-*p*-tolylsulfonyl amino acids, we are interested in investigating the effect of a second ligand on the structures of binary systems. Herein, we report a series of binary and ternary complexes constructed by lanthanide(III) centers, N-*p*-tolylsulfonyl amino acids and 2,2′-bipyridine, $[Ln_2L_6(H_2O)_4]_n$ (**1**) and $[LnL_3(bipy)(H_2O)]_2$ (**2a–b**, **3a–b**).

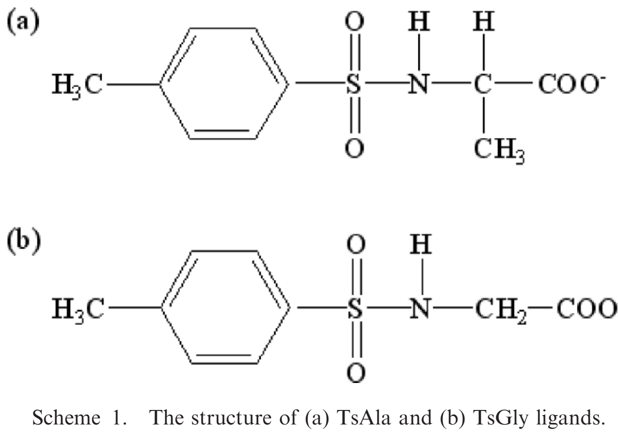
2. Experimental

2.1. *Materials and general methods*

N-*p*-tolylsulfonylglycine and N-*p*-tolysulfonylalanine (shown in scheme 1) were prepared according to literature procedures [15]; other reagents were purchased from the Shanghai Reagent Company. All reagents were of analytical grade and used without further purification. Elemental analyses of the complexes were performed on a Vario-EL elemental analyzer. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 360 FT-IR spectrometer using KBr pellets.

2.2. *Synthesis*

$[La_2(TsAla)_6(H_2O)_4]_n$ (1). Aqueous solutions of $LaCl_3$ were made by dissolving La_2O_3(1.629 g, 5 mmol) in an appropriate amount of hydrochloric acid and diluting to 10 mL. Then a solution (40 mL) of TsAla (2.673 g, 10 mmol) was added and the pH was carefully adjusted to 4–5 with 2 M NaOH. The reaction mixture was stirred at 70°C for



Scheme 1. The structure of (a) TsAla and (b) TsGly ligands.

12 h and then filtered. The filtrate was left at room temperature to evaporate the solvent. After several weeks, prismatic crystals were obtained. Anal. Calcd for $C_{60}H_{80}La_2N_6O_{28}S_6$(%): C, 40.06; H, 4.45; N, 4.67. Found: C, 39.86; H, 4.54; N, 4.50. IR (KBr pellet): 3256(m), 1538(vs), 1452(s), 1321(m), 1156(s), 817(m), 662(m).

[Gd(TsAla)$_3$(bipy)(H$_2$O)]$_2$ (2a). An aqueous mixture (50 mL) of $GdCl_3$ (10 mmol) and TsAla (2.434 g, 10 mmol) was stirred at 60°C for 3 h, then a solution (20 mL) of 2,2′-bipyridine (1.562 g, 10 mmol) was added and the pH was carefully adjusted to 4–5 with 2 M NaOH. The resulting solution was stirred for 24 h, then filtered. The filtrate was left to evaporate for about 15 days at room temperature to obtain colourless prismatic crystals. Anal. Calcd for $C_{80}H_{92}Gd_2N_{10}O_{26}S_6$(%): C, 45.40; H, 4.38; N, 6.62. Found: C, 45.34; H, 4.32; N, 6.67. IR (KBr pellet): 3454(m), 1665(vs), 1596(s), 1424(s), 1388(m), 1323(m), 1159(vs), 893(m), 766(m).

The syntheses of **2b** and **3a–b** were carried out similarly to **2a** except that TsAla ligand for **2a** is replaced by TsGly ligand in **3a–b**.

[Er(TsAla)$_3$(bipy)(H$_2$O)]$_2$ (2b). Anal. Calcd for $C_{80}H_{92}Er_2N_{10}O_{26}S_6$(%): C, 44.97; H, 4.34; N, 6.56. Found: C, 44.99; H, 4.27; N, 6.50. IR (KBr pellet): 3307(m), 1674(vs), 1596(s), 1434(s), 1388(m), 1332(m), 1159(vs), 893(m), 766(m).

[Er(TsGly)$_3$(bipy)(H$_2$O)]$_2$ (3a). Anal. Calcd for $C_{74}H_{80}Er_2N_{10}O_{26}S_6$(%): C, 43.31; H, 3.93; N, 6.82. Found: C, 43.44; H, 4.01; N, 6.60. IR (KBr pellet): 3259(m), 1681(vs), 1597(s), 1434(s), 1399(m), 1330(m), 1163(vs), 887(m), 764(m).

[Yb(TsGly)$_3$(bipy)(H$_2$O)]$_2$ (3b). Anal. Calcd for $C_{74}H_{80}N_{10}O_{26}S_6Yb_2$(%): C, 43.06; H, 3.91; N, 6.79. Found: C, 43.04; H, 3.94; N, 6.77. IR (KBr pellet): 3261(m), 1684(vs), 1598(s), 1433(s), 1400(m), 1331(m), 1161(vs), 885 (m), 764(m).

2.3. *X-ray crystallography*

The single crystals of complexes **1**, **2a–b** and **3a–b** with appropriate dimensions were mounted on a Bruker CCD diffractometer with a graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K, using ω and φ scan techniques. A self-consistent absorption correction of SADABS [16] based on Fourier coefficient fitting was applied. The crystal structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located based on difference Fourier synthesis coupled with geometrical analysis. All computations were performed on a PC computer using the programs of Bruker Smart and Bruker SHELXTL package [17, 18]. Crystallographic data are summarized in table 1, and selected bond lengths are listed in table 2 while selected hydrogen bond lengths and angles are presented in table 3.

3. Results and discussion

3.1. *Crystal structure*

X-ray structural analysis reveals that **1** adopts a chain structure with alternating two and four bridging TsAla ligands between adjacent La(III) centres. As shown

Table 1. Crystallographic data for compounds **1**, **2a**–**b** and **3a**–**b**.

Compound	**1**	**2a**	**2b**	**3a**	**3b**
CCDC deposit no.	CCDC-261017	CCDC-261016	CCDC-261014	CCDC-261015	CCDC-261018
Formula	$C_{60}H_{80}La_2N_6O_{28}S_6$	$C_{80}H_{92}Gd_2N_{10}O_{26}S_6$	$C_{80}H_{92}Er_2N_{10}O_{26}S_6$	$C_{74}H_{80}Er_2N_{10}O_{26}S_6$	$C_{74}H_{80}N_{10}O_{26}S_6Yb_2$
Fw	1803.48	2116.50	2136.52	2052.36	2063.92
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$/n	$P2_1/n$	$P2_1/n$	$P2_1$/n
a/Å	12.8689(18)	12.586(3)	12.5122(16)	12.2578(15)	12.2312(17)
b/Å	17.062(2)	18.397(4)	18.374(2)	19.037(3)	19.007(3)
c/Å	18.273(2)	19.526(4)	19.531(3)	17.952(2)	17.960(3)
$\alpha/^\circ$	89.114(3)	90.00	90.00	90.00	90.00
$\beta/^\circ$	74.763(3)	97.367(5)	97.156(2)	92.371(3)	92.318(2)
$\gamma/^\circ$	83.617(3)	90.00	90.00	90.00	90.00
V/Å^3	3846.7(9)	4483.8(18)	4455.2(10)	4185.5(9)	4172.0(10)
Z	2	2	2	2	2
D_{calcd}/g cm^{-3}	1.557	1.568	1.593	1.628	1.643
μ/mm^{-1}	1.339	1.687	2.092	2.224	2.461
θ range/°	2.02 to 27.55	1.82 to 27.55	1.83 to 27.53	1.97 to 27.52	1.56 to 27.51
R_1[a]	0.0366	0.0570	0.0314	0.0288	0.0245
wR_1[b]	0.0855	0.1317	0.0792	0.0641	0.0634

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. For **1,** $a = 0.0500$, $b = 0.0000$; for **2a**, $a = 0.0655$, $b = 5.6361$; for **2b**, $a = 0.0439$, $b = 2.2684$; for **3a**, $a = 0.0366$, $b = 0.0000$; for **3b**, $a = 0.0450$, $b = 0.0000$.

Table 2. Selected bond lengths (Å).

Compound **1**		Compound **2a**		Compound **2b**	
La(1)–O(1)	2.438(2)	Gd(1)–O(10)#1	2.330(3)	Er(1)–O(2)#1	2.241(2)
La(1)–O(5)	2.4780(19)	Gd(1)–O(9)	2.335(3)	Er(1)–O(6)#1	2.320(2)
La(1)–O(14)#1	2.4920(18)	Gd(1)–O(6)#1	2.349(3)	Er(1)–O(5)	2.322(2)
La(1)–O(10)#1	2.510(2)	Gd(1)–O(1)	2.374(3)	Er(1)–O(1)	2.327(2)
La(1)–O(9)	2.530(2)	Gd(1)–O(5)	2.376(3)	Er(1)–O(9)	2.359(2)
La(1)–O(13)	2.5813(19)	Gd(1)–O(1W)	2.496(3)	Er(1)–O(1W)	2.399(2)
La(1)–O(2W)	2.638(2)	Gd(1)–N(4)	2.576(3)	Er(1)–N(5)	2.522(2)
La(1)–O(1W)	2.646(2)	Gd(1)–N(5)	2.576(3)	Er(1)–N(4)	2.536(3)
La(1)–O(14)	2.7264(18)	Compound **3a**		Compound **3b**	
La(2)–O(21)	2.4486(19)	Er(1)–O(5)	2.286(2)	Yb(1)–O(6)#1	2.2233(19)
La(2)–O(2)	2.4665(19)	Er(1)–O(6)#1	2.305(2)	Yb(1)–O(9)	2.296(2)
La(2)–O(6)	2.4754(19)	Er(1)–O(2)#1	2.306(2)	Yb(1)–O(10)#1	2.3021(19)
La(2)–O(18)#2	2.4745(19)	Er(1)–O(1)	2.331(2)	Yb(1)–O(5)	2.3110(19)
La(2)–O(22)#2	2.532(2)	Er(1)–O(9)	2.334(2)	Yb(1)–O(1)	2.3383(18)
La(2)–O(17)	2.5519(19)	Er(1)–O(1W)	2.440(2)	Yb(1)–O(1W)	2.381(2)
La(2)–O(4W)	2.666(2)	Er(1)–N(5)	2.534(3)	Yb(1)–N(4)	2.510(2)
La(2)–O(3W)	2.6645(19)	Er(1)–N(4)	2.535(3)	Yb(1)–N(5)	2.514(2)

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1, -y, -z$; #2 $-x, -y, -z+1$; for **2a**: #1 $-x, -y+1, -z+3$; for **2b**: #1 $-x, -y+1, -z+1$; for **3a** and **3b**, #1 $-x+1, -y+4, -z$.

Table 3. Hydrogen bond lengths (Å) and bond angles (°).

D–H···A	d(D···A)	∠(DHA)	D–H···A	d(D···A)	∠(DHA)
Compound **1**			Compound **2b**		
O(1W)–H(1WA)···O(24)#3	3.454(4)	164.5	N(1)–H(1A)···O(10) #1	3.093(4)	145.6
O(1W)–H(1WB)···O(3W)	2.955(4)	146.8	N(2)–H(2B)···O(11))#2	3.073(6)	145.3
O(2W)–H(2WB)···O(11)#4	2.792(4)	162.3	N(3)–H(3D)···O(4) #1	3.057(5)	160.8
O(4W)–H(4WA)···O(5)	3.023(4)	148.1	Compound **3a**		
N(1)–H(1A)···O(17)	3.041(4)	161.9	O(1W)–H(1WA)···O(10)	2.660(3)	158.3
N(1)–H(1A)···O(17)	3.041(4)	161.9	O(1W)–H(1WB)···O(12)#2	2.938(3)	163.6
Compound **2a**			N(3)–H(3B)···O(7)#1	2.964(4)	166.5
N(1)–H(1A)···O(8) #1	3.062(5)	161.5	Compound **3b**		
N(2)–H(2B)···O(2) #1	3.111(5)	143.6	O(1W)–H(1WA)···O(2)	2.655(3)	159.2
N(3)–H(3D)···O(9))#2	3.073(7)	144.74	O(1W)–H(1WB)···O(3)#2	2.962(3)	154.0
			N(1)–H(1A)···O(12)#1	2.970(3)	166.2

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

in figure 1, the asymmetric comprises two crystallographically independent La(III) centres, which exhibit different coordination environments. La(1) adopts a capped square antiprism with seven carboxylate oxygen atoms from six TsAla ligands and two water molecules (La–O = 2.438(2) to 2.7264(18) Å) while La(2) centre is a distorted square antiprism with six carboxylate oxygen atoms from six TsAla ligands and two water molecules (La–O = 2.4486(19) to 2.666(2) Å). The TsAla ligands adopt bidentate and tridentate bridging modes in **1** which result in the different coordination environments of La(III). The alternation of two and four bridging TsAla ligands between adjacent La(III) centers gives a 1-D infinite chain. The La···La distances are 5.525(10) and 4.192(8) Å, very close to the Ln···Ln distance of a similar lanthanide chain complex of TsGly [14]. Figure 2 shows connection of adjacent chains connect via hydrogen bonds O(2W)–H(2WB)···O(11)#4 (2.792(4) Å)

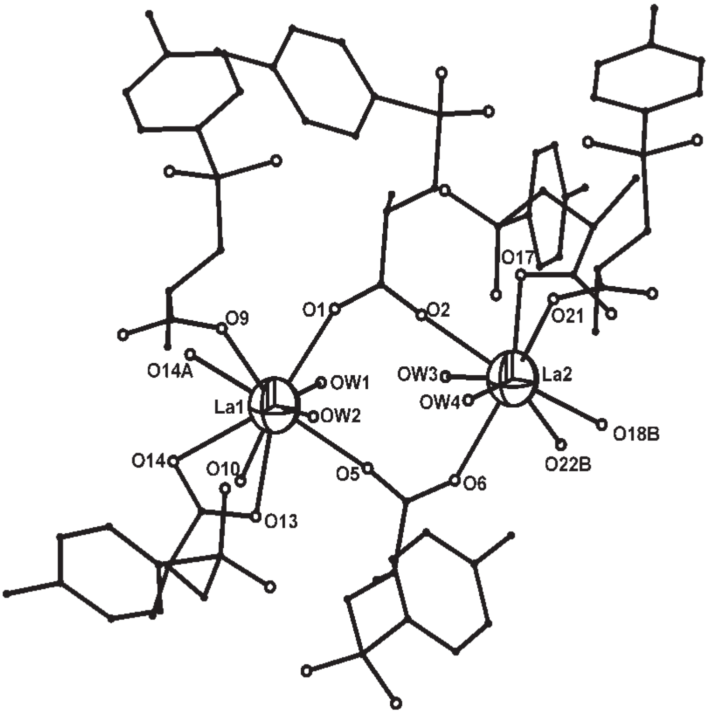


Figure 1. Perspective view of the coordination environment of the lanthanum in **1**.

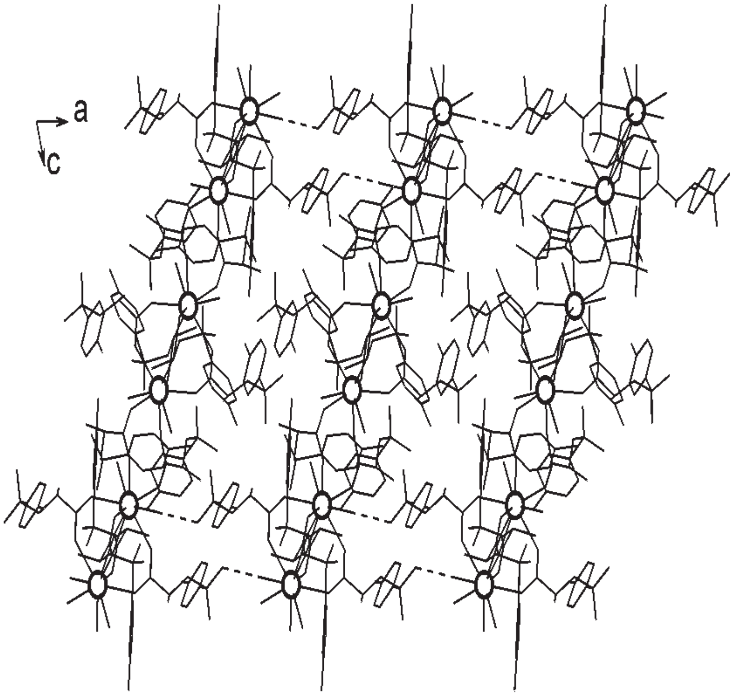


Figure 2. The two-dimensional layer structure of **1** constructed by hydrogen bond between chains.

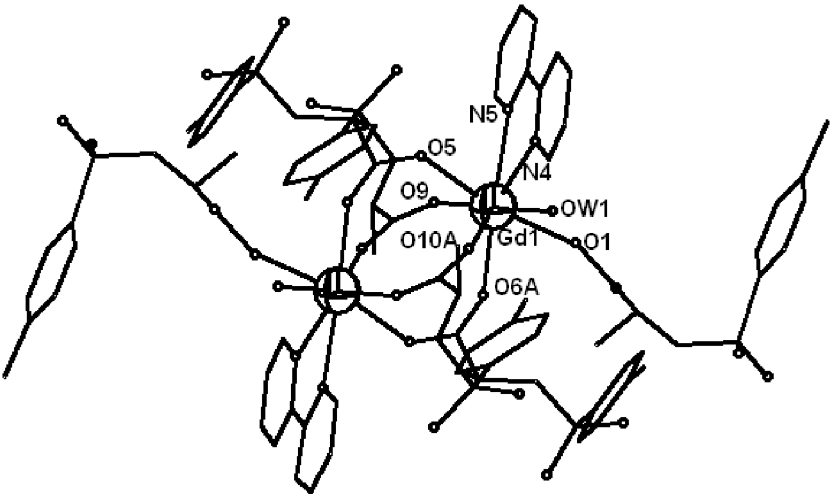


Figure 3. Perspective view of molecular structure of **2a** with selected atom-labeling and view of the coordination environment of gadolinium.

between carboxylate oxygen atoms of TsAla ligand and oxygen atoms of water forming the 2-D supramolecular network.

Some carboxylic acids, such as benzoic acid [19] and pyridine-4-carboxylic acid [20, 21], gave polymeric chain compounds when coordinating to lanthanide. While a second ligand, such as 2,2′-bipyridine or 1,10-phenanthroline, competes with the carboxylic acid for coordination, binuclear complexes were obtained [22–25]. Thus, after successfully synthesizing a series of binary complexes of lanthanide and N-*p*-tolylsulfonyl amino acids, we introduced 2,2′-bipyridine as a competing ligand for exploring whether 2,2′-bipyridine hinders chain extension. As expected, isostructural ternary complexes of lanthanide, N-*p*-tolylsulfonyl amino acids and 2,2′-bipyridine were obtained. The similar structures of **2a**–**b** and **3a**–**b**, can be adequately described by an example, **2a**. Compound **2a** features a dinuclear structure with the Gd(III) center eight-coordinated with five carboxylate oxygen atoms from five different TsAla ligands, two nitrogen atoms from one 2,2′-bipyridine a water (figure 3). The average distances of Gd–N, Gd–O (carboxylate) and Gd–O (water) are 2.576, 2.353 and 2.496 Å, respectively, comparable to similar lanthanide complexes with carboxylic acid and 2,2′-bipyridine [22–25]. In **2a**, four TsAla ligands adopt a bidentate bridging mode connecting two Gd(III) centres giving a dinuclear unit in which the Gd $\cdots$ Gd distance is 4.469(5) Å; the fifth TsAla is monodentate. Adjacent dinuclear units interact with each other through a number of hydrogen bonds (N(2)–H(2B) $\cdots$ O(2)#1, N(3)–H(3D) $\cdots$ O(9)#2) and π–π packing interactions between the benzene ring of TsAla giving a three-dimensional supermolecular structure (figure 4). The distances from the rings formed by C(14), C(15), C(16), C(17), C(18), C(19) and C(24), C(25), C(26), C(27), C(28), C(29) to the adjacent parallel benzene ring from the neighboring dinuclear unit are 3.474 and 3.518 Å. The crystal structure of compounds **2b** is similar to that of **2a**. In **2b**, the average distances of Er–N, Er–O (carboxyl) and Er–O (water) are 2.534, 2.312 and 2.440, respectively, while the Er $\cdots$ Er distance is 4.439(2) Å, slightly shorter than that of **2a**, attributable to

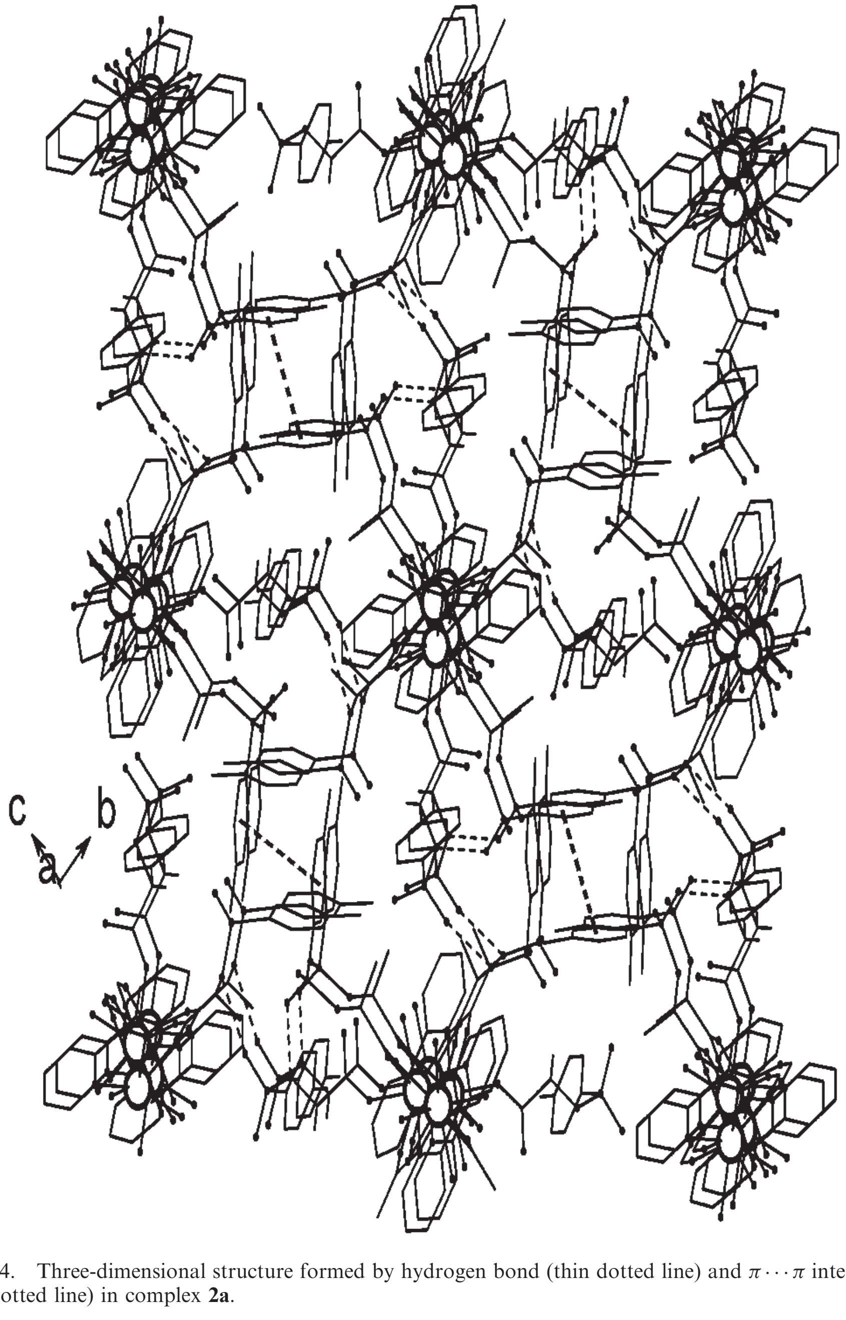


Figure 4. Three-dimensional structure formed by hydrogen bond (thin dotted line) and $\pi \cdots \pi$ interactions (thick dotted line) in complex **2a**.

lanthanide contraction. Under similar reaction conditions, except that TsAla ligand for **2a**–**b** is replaced by TsGly ligand, isostructural compounds **3a**–**b** were obtained, indicating that TsAla and TsGly have similar coordination behavior and the absence of the methyl group has no effect on the dinuclear structure established by TsAla ligand in **3a**–**b**.

3.2. *Infrared properties*

In the IR spectrum, the absence of any strong bands around 1719 cm^{-1} indicates that all carboxylic groups are deprotonated. A broad band near 3400 cm^{-1} can be attributed to the O–H vibration, revealing the presence of water in the compounds. The bands appearing at 1323–1332 and 1159–1161 cm^{-1} correspond to stretching vibrations of O=S=O. For **1**, the asymmetric and symmetric stretching vibration of the carboxylate group appear at 1538 and 1452 cm^{-1} while those of **2a**–**b** and **3a**–**b** fall in the ranges of 1596–1598, 1424–1434 and 1388–1400 cm^{-1}. The value of the difference $\Delta(\nu(COO)_{as} - \nu(COO)_{s})$ between the asymmetric and symmetric stretching modes of 200–170 cm^{-1} indicates that the carboxylate groups have different coordination modes, consistent with the structural analysis.

In conclusion, we have synthesized five lanthanide complexes with N-*p*-tolylsulfonyl amino acids and 2,2′-bipyridine as ligands. Compound **1** has a one-dimensional infinite chain structure. Introducing 2,2′-bipyridine into the binary system gave four new binuclear compounds **2a**–**b** and **3a**–**b,** indicating 2,2′-bipyridine plays the key role in transformation from chain to dinuclear structure.

Supplementary material

CCDC 261014–261018 (for **1**, **2a**–**b** and **3a**–**b**) contains the supplementary crystallographic data for this article. Copies of this information can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] T.G. Appleton, J.R. Hall, P.D. Prenzler. *Inorg. Chem.*, **28**, 815 (1989).
[2] H. Sigel, R.B. Martin. *Chem. Rev.*, **82**, 385 (1982).
[3] M. Sola. *Inorg. Chem.*, **35**, 4239 (1996).
[4] S. Chaudhuri. *J. Chem. Soc., Dalton Trans.*, **5**, 779 (1984).
[5] L. Antolini, L. Menabue, G.C. Pellacani, G.B. Gavioli, G. Grandi, L.P. Battaglia, A.B. Corradi, G. Marcotrigiano. *J. Chem. Soc., Dalton Trans.*, **8**, 1687 (1984).
[6] L. Antolini, L.P. Battaglia, G.B. Gavioli, A.B. Corradi, G. Marcotrigiano, L. Menabue, G.C. Pellacani. *J. Am. Chem. Soc.*, **105**, 4327 (1983).
[7] G.B. Gavioli, M. Borsari, L. Menabue, M. Saladini, M. Sola. *J. Chem. Soc., Dalton Trans*, **1**, 97 (1990).
[8] L. Antolini, L. Menabue, M. Sola, L.P. Battaglia, A.B. Corradi. *J. Chem. Soc., Dalton Trans*, **7**, 1367 (1986).
[9] A.B. Corradi, G. Lusvardi, L. Menabue, M. Saladini, P. Sgarabotto. *Polyhedron*, **18**, 1975 (1999).
[10] G.B. Gavioli, L. Menabue, M. Saladini, M. Sola, A.B. Corradi, L.P. Battaglia. *J. Chem. Soc., Dalton Trans.*, **7**, 1345 (1989).
[11] A.B. Corradi, E. Gozzoli, L. Menabue, M. Saladini, L.P. Battaglia, P. Sgarabotto. *J. Chem. Soc., Dalton Trans.*, **3**, 273 (1994).

[12] A.B. Corradi, L. Menabue, M. Saladini, M. Sola, L.P. Battaglia. *J. Chem. Soc., Dalton Trans.*, **17**, 2623 (1992).

[13] L. Menabue, M. Saladini, M. Sola. *Inorg. Chem.*, **29**, 1293 (1990).

[14] M.B. Zhang, Z.L. Chen, R.X. Hu, F.P. Liang, Z.Y. Zhou. *Chinese J. Chem.* (*in press*).

[15] E.W. McChesney, W. Kirk Swann. *J. Am. Chem. Soc.*, **59**, 1116 (1937).

[16] G.M. Sheldrick. *SADABS*, Siemens Analytical X-ray Instrument Division, Madison, WI (1995).

[17] G.M. Sheldrick. *SHELXL-97*, *Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).

[18] G.M. Sheldrick. *SHELXL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[19] A.W. Lam, W. Wong, S. Gao, G. Wen, X. Zhang. *Eur. J. Inorg. Chem.*, **1**, 149 (2003).

[20] B. Yan, Q.Y. Xie. *J. Mol. Struct.*, **688**, 73 (2004).

[21] L. Ma, O.R. Evans, B.M. Foxman, W.Lin. *Inorg. Chem.*, **38**, 5837 (1999).

[22] X. Li, L.P. Jin, X.J. Zheng, S.Z. Lu, J.H. Zhang. *J. Mol. Struct.*, **607**, 59 (2002).

[23] L. Jin, R, Wang, L. Li, S. Lu, S. Huang. *Polyhedron*, **18**, 376 (1999).

[24] A.M. Atria, R. Baggio, M.T. Garland, J.C. Muñoz, O. Peña. *Inorg. Chim. Acta*, **357**, 1997 (2004).

[25] J.S. Brodkin, B.M. Foxman. *Chem. Mater.*, **8**, 242 (1996).