

# 一种由 1,4,7-三氮杂环壬烷形成的三脚架配体及其与高氯酸钠组装的含 $[\text{Na}_4(\text{ClO}_4)_4]$ 四面体晶体结构

李秀敏 杨 雨 张宗尧\* 曹 睿

(中国人民大学化学系, 北京 100872)

**摘要:** 合成了一种多齿的三脚架配体: 三(2-(4,7-二甲磺酸基-1,4,7-三氮杂环壬烷基)甲基苯基)胺, 即  $\text{N}(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{-tacnTs}_2)_3$  (L), 其中 Ts=tosyl。它包含 3 个 1,4,7-三氮杂环壬烷连接在三苯基胺的邻位。该配体在高氯酸钠存在情况下结晶, 自组装得到 4 个钠离子形成的四面体结构晶体:  $[\text{Na}_4(\text{L})(\text{CH}_3\text{CN})(\text{ClO}_4)_4(\text{H}_2\text{O})_3]_n$ 。该晶体结构用 X 射线单晶衍射、粉末衍射、红外光谱和热重分析表征, 并用紫外吸收和荧光对其光学性质进行表征。

**关键词:** 晶体结构; 三脚架配体; 四面体; 二维框架; 三氮杂环壬烷基

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## A Tripodal Tris-tacn (tacn=1,4,7-Triazacyclononane) Ligand and Its Ability to Assemble a $[\text{Na}_4(\text{ClO}_4)_4]$ Tetrahedron Cluster

LI Xiu-Min YANG Yu ZHANG Zong-Yao\* CAO Rui

(Department of Chemistry, Renmin University of China, Beijing 100872, China)

**Abstract:** A multidentate tripodal ligand, tris(2-((4,7-ditosyl-1,4,7-triazonane-1-yl)methyl)benzyl)amine, namely  $\text{N}(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{-tacnTs}_2)_3$  (L, Ts=tosyl), which contains three triazacyclononane arms linked to the *ortho* positions of a tris(xylyl)amine scaffold, was synthesized. It stabilizes a  $[\text{Na}_4(\text{ClO}_4)_4]$  tetrahedron cluster, which is rarely reported in the literature. The resulted complex has the formula of  $[\text{Na}_4(\text{C}_{84}\text{H}_{102}\text{N}_{10}\text{O}_{12}\text{S}_6)(\text{CH}_3\text{CN})(\text{ClO}_4)_4(\text{H}_2\text{O})_3]_n$ . This tripodal tris-tacn complex has been characterized by single crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy and thermal thermogravimetric analysis. UV-visible absorption spectrum and fluorescence spectrum were measured to characterize the optical properties of the complex. CCDC: 1547366.

**Keywords:** crystal structure; tripodal ligand; tetrahedron cluster; two-dimensional framework; tacn

## 0 Introduction

Self-assembled coordination polymers have gained much attention due to their structural diversities, intriguing properties and applications in various fields. Coordination polymers reported so far present mainly polymeric structures with single metals or small

building blocks<sup>[1-6]</sup>. In order to make coordination polymers with more structural diversities, efforts have been made in ligand design, for example by introducing multi-dentate chelating groups to stabilize large high-nuclearity metal clusters as building blocks<sup>[7-9]</sup>. Transition metal elements have been mainly used<sup>[10-14]</sup>, while main group metal elements are less well-studied

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\*通信联系人。E-mail: zhangzongyaochem@ruc.edu.cn

because of their unpredictable coordination numbers owing to the lack of ligand field stabilization effect.

Tripodal ligands based on the tris(xylyl)amine backbone have been investigated, forming either convergent trinuclear metal complexes or divergent coordination complexes<sup>[15-16]</sup>. When three dipicolylamine units were attached to the tris(xylyl)amine scaffold, a tripodal ligand  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{N}(\text{CH}_2\text{Py})_2)_3$  (Py=pyridine) was formed. This ligand was used to synthesize and stabilize complexes containing  $\mu_3$ -oxoanion as reported by Lippard and co-workers<sup>[17-18]</sup>. Subsequently the tripodal ligand  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{N}(\text{CH}_2\text{Py})_2)_3$  was reported in the synthesis of a trinuclear zinc complex for carbon dioxide fixation<sup>[19]</sup>. Most recently, a tripodal tris-tacn ligand,  $N(\text{CH}_2\text{-}m\text{-C}_6\text{H}_4\text{-CH}_2\text{tacn})_3$  was reported to form a nano-sized coordination cage with 30 Ni(II) ions<sup>[20]</sup>.

Herein, we report a multidentate tripodal ligand,  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{tacnTs}_2)_3$  (L), and its ability to assemble a  $[\text{Na}_4(\text{ClO}_4)_4]$  tetrahedron cluster. The stabilized  $[\text{Na}_4(\text{ClO}_4)_4]$  tetrahedron cluster is rarely reported in the literature. Ligand L has been fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectroscopy and elemental analysis. The resulted complex **1**,  $[\text{Na}_4(\text{C}_{84}\text{H}_{102}\text{N}_{10}\text{O}_{12}\text{S}_6)(\text{CH}_3\text{CN})(\text{ClO}_4)_4(\text{H}_2\text{O})_3]_n$  has been thoroughly characterized by single crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy and thermogravimetric analysis. UV-visible absorption spectrum and fluorescence spectrum were measured to characterize its optical properties.

## 1 Experimental

### 1.1 Materials and general methods

Manipulations of air- and moisture-sensitive materials were performed under an atmosphere of nitrogen gas using standard Schlenk line techniques. All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Dry solvents, including acetonitrile, and dichloromethane, were purified by passage through activated alumina. The compounds  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CHO})_3$  and  $\text{tacnTs}_2$  were synthesized according to methods reported previously<sup>[14]</sup>.  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements

were made on a Bruker spectrometer operating at 400 MHz. MALDI-TOF mass spectra was acquired on a Bruker Daltonics Inc. BIFLEX III matrix-assisted laser desorption/ionization time of flight mass spectrometer. Powder X-ray diffraction was made using X-ray diffractometer (Shimadzu, XRD-7000) with Cu  $K\alpha$  as X-ray radiation ( $\lambda=0.154$  18 nm,  $U=40$  kV,  $I=30$  mA,  $2\theta=5^\circ\sim 50^\circ$ ). Thermogravimetric data were collected on a TA Q50 analyzer in nitrogen at heating rate of  $10$   $^\circ\text{C}\cdot\text{min}^{-1}$ . The infrared spectra (2% sample in KBr pellet) was recorded on a Bruker spectrophotometer (OPUS software). UV-visible absorption spectra were recorded on a Hitachi U-3900H absorption spectrophotometer at room temperature in thin dichloromethane solution. Fluorescence spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer at room temperature.

### 1.2 Synthesis of $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{tacnTs}_2)_3$

Compound  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CHO})_3$  (370.0 mg, 0.1 mmol) was dissolved in dichloromethane (5 mL), to which  $\text{tacnTs}_2$  (131.0 mg, 0.3 mmol) and  $\text{NaBH}(\text{OAc})_3$  (101.0 mg, 0.48 mmol) were added. The reaction mixture was stirred 24 h under Ar and then was neutralised with saturated  $\text{NaHCO}_3$  solution. The organic phase was separated and the aqueous phase was further extracted with dichloromethane (20 mL). The resulting crude reaction mixture was dried and purified by preparative chromatography ( $V_{\text{ethyl acetate}}/V_{\text{hexane}}=1:1$ ) affording a pure pink solid (42 mg, Yield: 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.39 (s, 18H), 2.65 (s, 12H), 2.95 (s, 12H), 3.36 (s, 12H), 3.45 (s, 6H), 3.56 (s, 6H), 7.10~7.50 (m, 24H), 7.60 (d, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.73, 51.73, 52.57, 54.81, 56.23, 57.27, 126.79, 127.43, 129.95, 130.00, 130.41, 131.55, 135.50, 138.03, 139.07, 143.52. Anal. Calcd. for  $\text{C}_{84}\text{H}_{102}\text{N}_{10}\text{O}_{12}\text{S}_6$ (%): C, 61.66; H, 6.28; N, 8.56. Found(%): C, 61.89; H, 6.41; N, 8.78. MALDI-TOF-MS for  $[\text{M}+\text{Na}]^+$ : Calcd. 1 657.6; Found, 1 657.6

### 1.3 Synthesis of complex 1

Ligand  $N(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{-CH}_2\text{tacnTs}_2)_3$  (16 mg, 0.01 mmol) was dissolved in acetonitrile (3 mL). To this solution,  $\text{NaClO}_4$  (5.6 mg, 0.04 mmol) dissolved in water (2 mL) was then added. The colorless solution was

stirred overnight and was then filtered. Slow evaporation of the filtration afforded colourless prismatic crystals of complex **1** (10.6 mg, Yield: 42.7%), which were suitable for single crystal X-ray diffraction analysis. Anal. Calcd. for C<sub>86</sub>H<sub>111</sub>Cl<sub>4</sub>N<sub>11</sub>Na<sub>4</sub>O<sub>31</sub>S<sub>6</sub>(%): C, 46.51; H, 5.04; N, 6.94. Found(%): C, 46.26; H, 5.00; N, 6.49.

#### 1.4 Crystal structure determination

Colorless block single crystal sample of complex **1**, with dimensions of 0.10 mm×0.12 mm×0.18 mm suitable for X-ray analysis was coated with Paratone-N oil, suspended in a small fiber loop, and placed in a cold gaseous nitrogen stream on a Bruker D8 VENTURE X-ray diffractometer performing  $\varphi$ - and  $\omega$ -scans at 100(2) K. Diffraction intensities were measured using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm). Data collection, indexing, initial cell

refinements, frame integration, and final cell refinements were accomplished using the program APEX2. Data reduction and empirical absorption correction were performed using the SAINT and SADABS program<sup>[21]</sup>. The structures were solved by the direct method using SHELXS<sup>[22]</sup> and refined by full-matrix least squares on  $F^2$  using SHELXL<sup>[23]</sup>. Crystal data, data collection and structure refinement details were summarized in Table 1. The C-bound H atoms were placed in calculated positions and treated using a riding-model approximation, with C-H 0.093 nm and C-H 0.097 nm for methylene H atoms and O-H 0.085 nm for coordinated water H atoms, and refined as riding, with  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C}, \text{O})$ .

CCDC: 1547366.

Table 1 Crystal data and structure parameters for the complex **1**

Formula	C <sub>86</sub> H <sub>111</sub> Cl <sub>4</sub> N <sub>11</sub> Na <sub>4</sub> O <sub>31</sub> S <sub>6</sub>	$\mu / \text{mm}^{-1}$	0.35
Formula weight	2 220.97	$F(000)$	6 960
Crystal system	Trigonal	$\theta_{\text{min}}, \theta_{\text{max}} / (^\circ)$	1.50, 24.50
Space group	$R\bar{3}$	Goodness of fit on $F^2$	1.024
$a / \text{nm}$	1.903 24(6)	Reflections collected	9 911
$b / \text{nm}$	1.903 24(6)	Independent reflections ( $R_{\text{int}}$ )	5 665 (0.046 5)
$c / \text{nm}$	4.737 8(3)	$R_1, wR_2 [I > 2\sigma(I)]$	0.047 1, 0.125 1
$V / \text{nm}^3$	14.862 6(12)	$R_1, wR_2$ (all data)	0.057 5, 0.134 3
$Z$	6	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	850, -750

## 2 Results and discussion

### 2.1 Crystal structure description

Ligand L was synthesized according to the reaction depicted in Fig.1. Its identity and purity were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR measurements. In the presence of NaClO<sub>4</sub>, crystal growth of L gave complex

**1**, which crystallizes in the trigonal space group  $R\bar{3}$ . The asymmetric unit contains one third of the ligand L, one Na and one perchlorate anion. Ball-and-stick structural representation of the whole complex is shown in Fig.2. There are four Na atoms forming a tetrahedron. The Na<sub>4</sub> tetrahedron is located in the shell cavity of the ligand, and the coordination

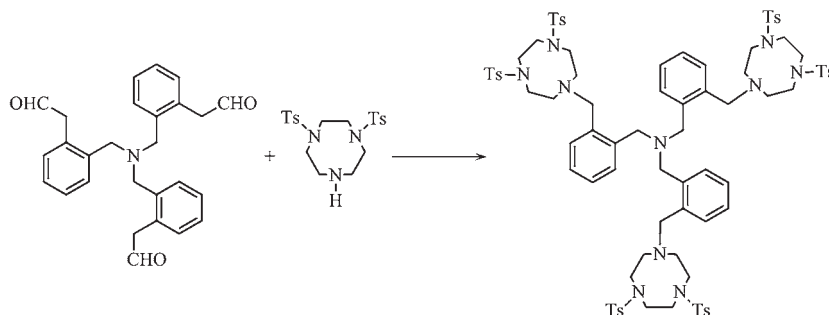
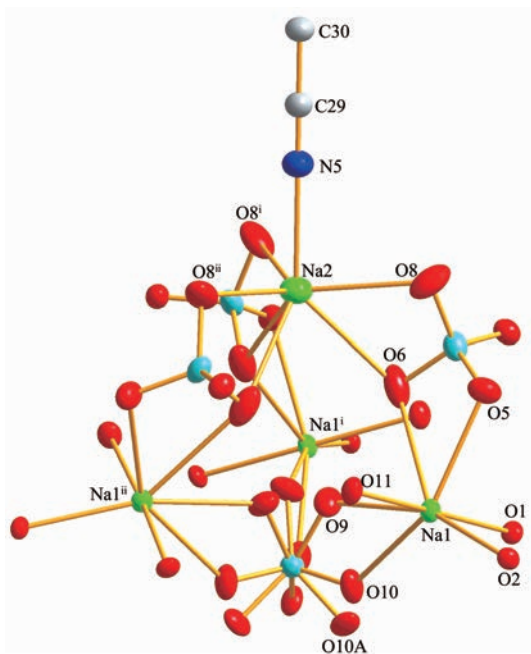


Fig.1 Synthesis of ligand L

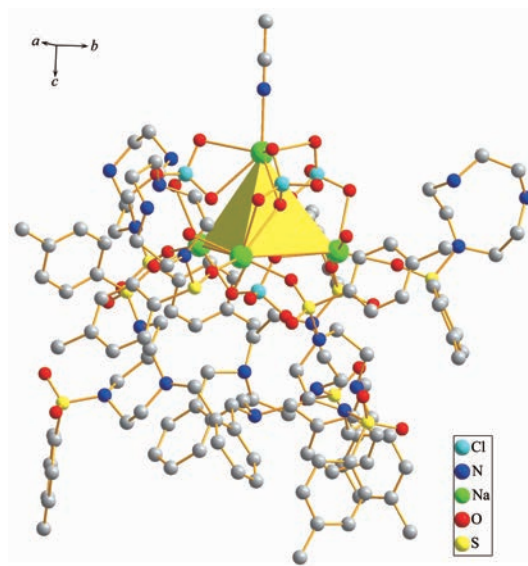
environment of Na cores is shown in Fig.3. Owing to the  $C_3$ -axis, three basal Na atoms lie on an equilateral triangle plane with  $\text{Na}\cdots\text{Na}$  distance of 0.543 3(3) nm. The distance between the apical Na and the basal Na is 0.491 9(2) nm. The dihedral angle between lateral face and base is  $67.510 (27)^\circ$ . The apical Na2 is seven-coordinated with three symmetrical equivalent O6 and three symmetrical equivalent O8 from the perchlorate, namely O6, O6<sup>i</sup>, O6<sup>ii</sup>, O8, O8<sup>i</sup> and O8<sup>ii</sup>, (Symmetry codes: <sup>i</sup>  $-y, x-y, z$ ; <sup>ii</sup>  $y-x, -x, z$ ) and a N atom from solvent acetonitrile. The basal Na1 is also seven-coordinated with two O atoms from the previous perchlorate moiety, two atoms from the disordered basal perchlorate, two O atoms from the tosyl group and one O atom from solvent water molecule.



Atomic displacement ellipsoids depicted at 30% probability level; Hydrogen atoms and some atom labels are omitted for clarity; Symmetry codes: <sup>i</sup>  $-x+1, -y+1, -z+1$ ; <sup>ii</sup>  $-x+y, -x+1, z$

Fig.2 Atom labelling scheme showing the coordination environment for the  $\text{Na}^+$  cations of complex **1**

The charge is balanced by four  $\text{ClO}_4^-$  counter anions, which connect the Na cores. There is one  $\text{ClO}_4^-$  located below the plane created by three symmetrical equivalent Na1, with  $C_3$ -axis passing through is rotationally disordered. For atom O10, the free variable refinements give the occupancy of 0.7 at the site of O10, and the occupancy of 0.3 at the site of



Hydrogen atoms are omitted for clarity

Fig.3 Extended structure of complex **1** drawn in ball-and-stick mode

O10A. However, atom O9 should lie on the special position that  $C_3$ -axis is passing through. The rotational disorder makes it difficult to fix O9 on that location. Therefore, O9 is refined with an occupancy of 0.33, and after symmetry operations, the occupancy of the O9 atom and the chemical composition is correct. The other three perchlorate ions are symmetrical equivalent. Each of those perchlorate ions combines an apical Na atom and a basal Na atom, with O6 bridging them directly with Na-O bond distances of 0.275 0(4) nm and 0.265 3(4) nm, which consists the  $\text{Na}_4$  tetrahedron cluster structure shown in Fig.2. These  $\text{Na}_4$  clusters are jointly connected by Na-O bonds. As mentioned above, each basal Na atom is coordinated by two tosyl O atoms, with three symmetrical O1 from one ligand molecule and three O2 from three separate ligand molecules. Though there are not any direct bridging atom, the tosyl group bridges the two  $\text{Na}_4$  clusters. Through those interactions, the 2D framework is built up. The structure is further stabilized by hydrogen bonds. Water atom O11 is a donor to atom O3<sup>i</sup>, respectively (Table 2).

## 2.2 PXRD, IR and optical properties

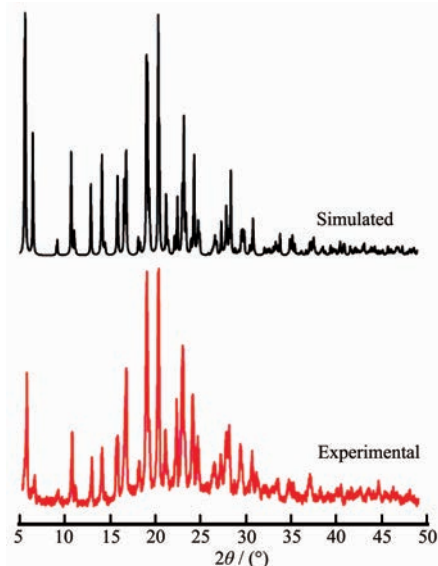
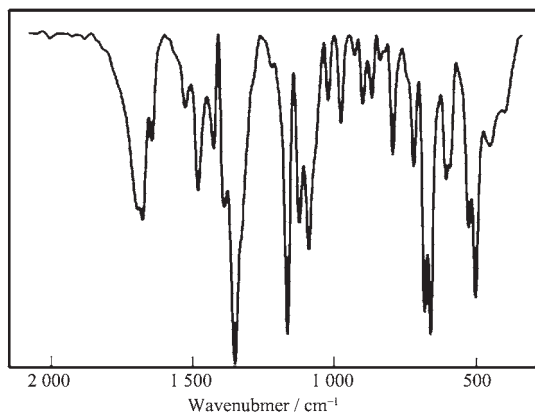
Powder X-ray diffraction analysis is also applied to further analyze the bulky sample. As is shown in Fig.4, the experimental powder peaks fit the simulated

**Table 2 Hydrogen-bond geometry for complex 1**

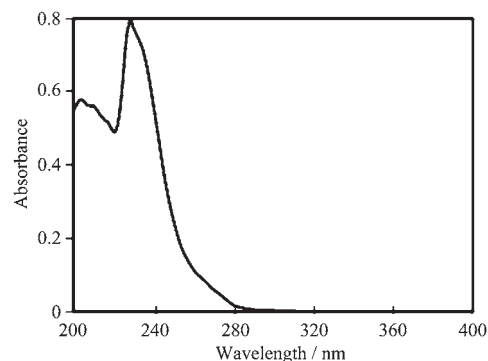
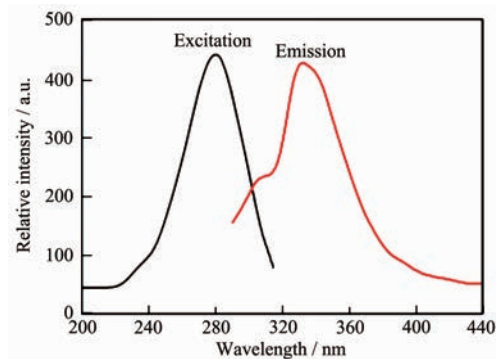
D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H...A}) / \text{nm}$	$d(\text{D...A}) / \text{nm}$	$\angle \text{D-H...A} / (^\circ)$
O11-H11B...O3 <sup>i</sup>	0.085(1)	0.212(1)	0.296 9(3)	17.6(5)

Symmetry codes: <sup>i</sup>  $-x+1, -y+1, -z+1$ 

powder patterns from the single crystal data very well. In addition, infrared spectrum is also used to analyze the complex, confirming very strong characteristic absorption peaks of perchlorate ions at  $1\ 067\ \text{cm}^{-1}$  (Fig.5)<sup>[24]</sup>. Optical properties of the complex **1** have been studied at room temperature. The UV-visible absorption spectrum of complex **1** in dichloromethane shows intense absorption events with peaks at 210 and 230 nm (Fig.6). It can be attributed to the  $n\text{-}\sigma^*$  and  $\pi\text{-}\pi^*$  electronic transition of the ligand. The excitation spectrum of complex **1** exhibits a broad band from 230 to ~320 nm with the strongest peak at

Fig.4 PXRD pattern of complex **1**Fig.5 FTIR spectrum of complex **1**

280 nm. The emission spectrum has  $\lambda_{\text{em,max}} = 335\ \text{nm}$  (Fig.7), which might be attributed to the inter ligand charge transfer.

Fig.6 UV-visible absorption spectrum of complex **1** in dichloromethane at room temperatureFig.7 Excitation and emission spectra of complex **1** in dichloromethane at room temperature

### 2.3 Thermal analysis

Furthermore, elementary analysis is applied using bulk crystalline samples. However, the percentage of N is slightly lower than expected. We suspect that the bound MeCN molecule is readily dissociated. Therefore, thermal gravimetric analyses (TGA) were performed from 20 to 800 °C (Fig.8). The first weight loss of 4.96% is in the range from 54 to 213 °C, corresponding to the removal of three coordinated water molecule and one coordinated MeCN molecule (Calcd. 4.31%). This phenomenon is in consistent with the results of elemental analysis. Upon further heating, an obvious weight loss occurs in the temperature

range of 210~370 °C, corresponding to the release of ligands. After 370 °C, no weight loss is observed, indicating the complete decomposition of complex **1**.

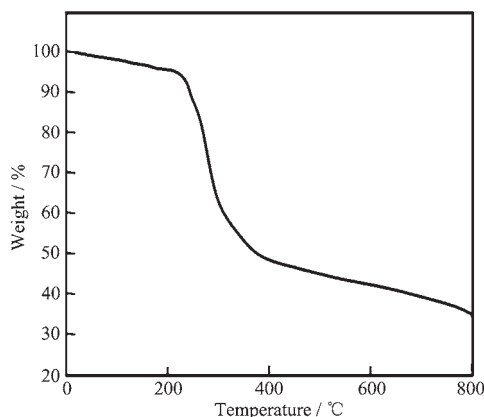


Fig.8 TGA curve of complex **1**

### 3 Conclusions

In conclusion, a multidentate tripodal ligand  $N(CH_2O-C_6H_4-CH_2-tacnTs_2)_3$  was synthesized and was used to stabilize a  $[Na_4(ClO_4)_4]$  tetrahedron cluster. This tripodal tris-tacn complex has been characterized by single crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy and thermogravimetric analysis. UV-visible absorption spectrum and fluorescence spectrum were measured to characterize its optical properties. Such a  $[Na_4(ClO_4)_4]$  tetrahedron cluster is rarely reported in the literature. This work highlights the value of tripodal ligands derived from tris(xylyl)amine backbone in assembling metal clusters with  $C_3$  symmetry.

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