研究简报

# 由氨基酸配位的铜修饰十二核钨单元构成的一维链状化合物$(H_3O)_3\{[Na_3(H_2O)_{13}][(Cu(Gly)_2)_2(H_2W_{12}O_{42})]\}\cdot 11H_2O$

吴小园 张全争 何 翔 陈淑妹 杨文斌 卢灿忠*
(中国科学院福建物质结构研究所,结构化学国家重点实验室,福州 350002)

**关键词**: 有机无机杂化材料; 水热合成; 晶体结构; 钨多酸; 氨基酸
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## One-dimensional Chain Polyoxotungstate Decorated with Amino Acid Copper Complex: $(H_3O)_3\{[Na_3(H_2O)_{13}][(Cu(Gly)_2)_2(H_2W_{12}O_{42})]\}\cdot 11H_2O$

WU Xiao-Yuan ZHANG Quan-Zheng HE Xiang CHEN Shu-Mei YANG Wen-Bin LU Can-Zhong*
(*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou* 350002)

**Abstract:** A new compound, $(H_3O)_3\{[Na_3(H_2O)_{13}][(Cu(Gly)_2)_2(H_2W_{12}O_{42})]\}\cdot 11H_2O$ (**1**), has been synthesized and structurally characterized, which represents the first example of a polyoxotungstate-surface being decorated with amino acid ligand. Two *cis*-$\{Cu(Gly)_2\}^{2+}$ engraft into the $(H_2W_{12}O_{42})^{10-}$ with Cu-O bond of 0.241 2(7) nm, and $Na^+$ ions linked these $[(Cu(Gly)_2)_2(H_2W_{12}O_{42})]^{6-}$ clusters into a one-dimensional chain. CCDC: 278000.

**Key words:** organic-inorganic hybrid; hydrothermal synthesis; crystal structure; polyoxotungstate; amino acid

The design and synthesis of organic-inorganic hybrid compounds have aroused contemporary interest; not only owing to their diverse structures, but also to their potential applications in fields such as catalysis, medicine, analytical chemistry and photochemistry[1,2].

In polyoxometalate (POM) chemistry, a brand-new branch is of the decoration on polyoxoanions with various transition metal complexes or organic moieties[3]. Such kinds of decorated POM derivatives will merge remarkable features of organic ligands coordinated transition metals and of POMs. To date, a number of such materials constructed from vanadium and molybdenum isopolyanions have been reported[4]. However, examples of tungsten oxides as inorganic components are rather limited and have been much concentrated on the compounds with organic amines as ligands, such as $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$[5], $\{PW_9V_3O_{40}[Ag(2,2'\text{-bipy})]_2[Ag_2(2,2'\text{-bipy})_3]_2\}$[6], $[\{Cu(en)_2\}_4Cu(H_2O)_2H_2W_{12}O_{42}]\cdot H_2O$[7] and $[Cu(en)_2(H_2O)][\{Cu(en)_2\}_2SiW_{11}CuO_{39}]\cdot 7H_2O$[8]. On the other hand, amino acids, as a good bridging ligand for building organic-inorganic hybrid materials, have attracted an increasing interest in recent years not only due to their vari-

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*通讯联系人。E-mail:czlu@fjirsm.ac.cn
第一作者:吴小园,女,28 岁,在读博士;研究方向:多酸化学。

ous coordination types, but also their important roles in the biochemical activity. Several POMs with amino acids have been reported recently, most of them were of polyoxomolybdates[9~12]. To our knowledge, there are only two examples of polyoxotungstates[13,14], in which amino acid acts as ions for charge balance. However, polyoxotungstates based compound decorated by amino acid has not been reported to date. Here we report a new compound $(H_3O)_3\{[Na_3(H_2O)_{13}][(Cu(Gly)_2)_2(H_2W_{12}O_{42})]\}\cdot 11H_2O$ (**1**), which contains paradodecatungstate-B unit decorated by $[Cu(Gly)_2]^{2+}$ groups.

## 1 Experimental section

### 1.1 Physical measurements

All reagents are analytical grade and used without further purification. Infrared spectra was recorded on Magna 750 FTIR spectrometer using KBr pellets. C, H, N and O microanalysis was carried out on Vario ELШ elemental analyzer. Thermogravimetric analysis was performed on a NETZSCH STA 449C instrument.

### 1.2 Preparation

A solution of $Na_2WO_4\cdot 2H_2O$ (1.0 mmol), glycine (2.0 mmol), $CuCl_2\cdot 2H_2O$ (1.0 mmol) and $H_2O$ (10 mL) was stirred at room temperature, and the pH of mixture was adjusted to 5.5 with diluted NaOH solution. The resulting suspension was sealed in a 25 $cm^3$ Teflon-lined reactor, which was kept at 140 ℃ for 3 days. Blue block crystals of **1** were isolated from filtrate after two weeks, washed with distilled water and dried in air (Yield 48%, based on W). Element analysis for **1** Calcd. (%): C: 2.49, H: 1.96, N: 1.45, O: 31.90; Found (%): C: 2.47,H: 2.05, N: 1.43, O: 31.95. IR ($cm^{-1}$, KBr): 3 414(s), 1 638(s), 1 618(s), 1 385(m), 1 122(m), 938(m), 869(m), 704(m), 619(m).

### 1.3 X-ray crystallography

Suitable single crystal with approximate dimensions (0.28 mm × 0.15 mm × 0.13 mm) was used for X-ray diffraction analysis. The data collection was performed at 293 K on a Mercury CCD Diffractometer equipped with a graphite monochromator with Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm). Empirical absorption correction was applied by using the SADABS program[15]. The structure was solved with direct methods and all calculations were performed using the SHELXTL package[16]. The structure was refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. Some of the water molecules are disordered. All hydrogen atoms were generated geometrically and were constrained to ride on their respective parent atoms with C-H=0.097 nm, N-H=0.090 nm, O-H=0.085 nm, $U_{iso}$=1.2 $U_{eq}$. Details of the crystal data are listed in Table 1. Selected bond lengths and angles are listed in Table 2 and Table 3, respectively.

CCDC: 278000.

**Table 1 Crystal data and structure refinement parameters for compound 1**

| | | | |
|---|---|---|---|
| Empirical formula | $C_8H_{75}Cu_2N_4Na_3O_{77}W_{12}$ | Absorption coefficient / $mm^{-1}$ | 16.327 |
| Formula weight | 3 861.97 | $F(000)$ | 3492 |
| Crystal system | Monoclinic | Crystal size / mm | 0.28 × 0.15 × 0.13 |
| Space group | $P2_1/m$ | $\theta$ range for data collection / (°) | 3.04 to 27.48 |
| $a$ / nm | 1.254 18(6) | Limiting indices | $-15 \leqslant h \leqslant 6$, $-30 \leqslant k \leqslant 29$, $-19 \leqslant l \leqslant 19$ |
| $b$ / nm | 2.373 07(13) | Reflections collected / unique | 33 471 / 10 216 [$R_{int}$=0.048 1] |
| $c$ / nm | 1.479 53(8) | Data / restraints / parameters | 10 216 / 0 / 489 |
| $\beta$ / (°) | 97.231(3) | Goodness-of-fit on $F^2$ | 1.09 |
| Volume / $nm^3$ | 4.368 4(4) | Final $R$ indices [$I>2\sigma(I)$] | $R_1$=0.042 7, $wR_2$=0.114 9 |
| $Z$ | 2 | $R$ indices (all data) | $R_1$=0.047 6, $wR_2$=0.118 6 |
| Calculated density / ($Mg\cdot m^{-3}$) | 2.936 | | |

**Table 2 Selected bond lengths (nm) for compound 1**

| | | | | | |
|---|---|---|---|---|---|
| Na(1)-O(26) | 0.235 2(13) | Cu(7)-N(6) | 0.195 9(9) | W(3)-O(18)#2 | 0.224 8(6) |
| Na(1)-O(23) | 0.239 1(7) | Cu(7)-O(3) | 0.196 3(7) | W(4)-O(22) | 0.172 7(6) |
| Na(1)-O(23)#1 | 0.239 1(7) | Cu(7)-O(9) | 0.241 2(7) | W(4)-O(6)#2 | 0.177 7(6) |

Continued Table 2

| | | | | | |
|---|---|---|---|---|---|
| Na(1)-O(27)#1 | 0.241 1(9) | W(1)-O(10) | 0.174 7(6) | W(4)-O(18)#2 | 0.189 3(6) |
| Na(1)-O(27) | 0.241 1(9) | W(1)-O(9) | 0.175 8(6) | W(4)-O(21) | 0.195 5(6) |
| Na(1)-O(28) | 0.244 1(16) | W(1)-O(7) | 0.187 7(6) | W(4)-O(14) | 0.209 8(6) |
| Na(2)-O(29)#1 | 0.240 0(10) | W(1)-O(5) | 0.193 9(6) | W(4)-O(13) | 0.223 8(5) |
| Na(2)-O(29) | 0.240 0(10) | W(1)-O(6) | 0.222 0(6) | W(5)-O(23) | 0.171 7(6) |
| Na(2)-O(30) | 0.240 1(13) | W(1)-O(8) | 0.223 9(6) | W(5)-O(16) | 0.179 9(6) |
| Na(2)-O(31) | 0.240 9(10) | W(2)-O(25) | 0.1737(6) | W(5)-O(8) | 0.190 8(5) |
| Na(2)-O(31)#1 | 0.240 9(10) | W(2)-O(24) | 0.175 3(7) | W(5)-O(21) | 0.194 5(6) |
| Na(2)-O(32) | 0.244 6(15) | W(2)-O(17) | 0.190 4(6) | W(5)-O(11) | 0.208 6(6) |
| Na(3)-O(34) | 0.233(2) | W(2)-O(5) | 0.1911(6) | W(5)-O(13) | 0.225 5(5) |
| Na(3)-O(35) | 0.239(2) | W(2)-O(8) | 0.226 6(6) | W(6)-O(15) | 0.173 0(6) |
| Na(3)-O(33) | 0.241(3) | W(2)-O(18) | 0.227 8(5) | W(6)-O(11) | 0.185 5(6) |
| Na(3)-O(15)#1 | 0.242 3(6) | W(3)-O(19) | 0.1741(6) | W(6)-O(14) | 0.186 1(6) |
| Na(3)-O(15) | 0.242 3(6) | W(3)-O(20) | 0.174 6(6) | W(6)-O(7) | 0.195 1(6) |
| Na(3)-O(30) | 0.256 8(16) | W(3)-O(12) | 0.187 7(6) | W(6)-O(12) | 0.196 4(6) |
| Cu(7)-O(1) | 0.193 9(8) | W(3)-O(17)#2 | 0.195 8(6) | W(6)-O(13) | 0.225 1(6) |
| Cu(7)-N(5) | 0.195 5(9) | W(3)-O(16)#2 | 0.217 6(6) | | |

**Table 3 Selected bond angles (°) for compound 1**

| | | | | | |
|---|---|---|---|---|---|
| O(10)-W(1)-O(9) | 102.1(3) | O(19)-W(3)-O(16)#2 | 88.7(3) | O(8)-W(5)-O(13) | 85.9(2) |
| O(10)-W(1)-O(7) | 97.5(3) | O(20)-W(3)-O(16)#2 | 168.5(3) | O(21)-W(5)-O(13) | 70.9(2) |
| O(9)-W(1)-O(7) | 98.7(3) | O(12)-W(3)-O(16)#2 | 85.3(2) | O(11)-W(5)-O(13) | 72.3(2) |
| O(10)-W(1)-O(5) | 95.5(3) | O(17)#2-W(3)-O(16)#2 | 79.0(2) | O(15)-W(6)-O(11) | 102.4(3) |
| O(9)-W(1)-O(5) | 97.7(3) | O(19)-W(3)-O(18)#2 | 163.9(3) | O(15)-W(6)-O(14) | 102.4(3) |
| O(7)-W(1)-O(5) | 156.4(2) | O(20)-W(3)-O(18)#2 | 92.4(3) | O(11)-W(6)-O(14) | 93.2(3) |
| O(10)-W(1)-O(6) | 167.8(3) | O(12)-W(3)-O(18)#2 | 86.3(2) | O(15)-W(6)-O(7) | 100.8(3) |
| O(9)-W(1)-O(6) | 89.3(3) | O(17)#2-W(3)-O(18)#2 | 73.2(2) | O(11)-W(6)-O(7) | 87.5(3) |
| O(7)-W(1)-O(6) | 84.7(2) | O(16)#2-W(3)-O(18)#2 | 76.6(2) | O(14)-W(6)-O(7) | 156.1(3) |
| O(5)-W(1)-O(6) | 78.7(2) | O(22)-W(4)-O(6)#2 | 104.2(3) | O(15)-W(6)-O(12) | 100.8(3) |
| O(10)-W(1)-O(8) | 91.1(3) | O(22)-W(4)-O(18)#2 | 103.0(3) | O(11)-W(6)-O(12) | 156.0(2) |
| O(9)-W(1)-O(8) | 164.9(3) | O(6)#2-W(4)-O(18)#2 | 96.0(3) | O(14)-W(6)-O(12) | 87.4(3) |
| O(7)-W(1)-O(8) | 86.7(2) | O(22)-W(4)-O(21) | 97.5(3) | O(7)-W(6)-O(12) | 82.5(3) |
| O(5)-W(1)-O(8) | 73.4(2) | O(6)#2-W(4)-O(21) | 92.5(3) | O(15)-W(6)-O(13) | 178.7(3) |
| O(6)-W(1)-O(8) | 77.1(2) | O(18)#2-W(4)-O(21) | 155.1(2) | O(11)-W(6)-O(13) | 76.6(2) |
| O(25)-W(2)-O(24) | 103.9(3) | O(22)-W(4)-O(14) | 93.1(3) | O(14)-W(6)-O(13) | 76.8(2) |
| O(25)-W(2)-O(17) | 96.4(3) | O(6)#2-W(4)-O(14) | 162.4(3) | O(7)-W(6)-O(13) | 80.1(2) |
| O(24)-W(2)-O(17) | 100.3(3) | O(18)#2-W(4)-O(14) | 83.1(2) | O(12)-W(6)-O(13) | 80.2(2) |
| O(25)-W(2)-O(5) | 99.6(3) | O(21)-W(4)-O(14) | 81.8(2) | W(2)-O(5)-W(1) | 118.1(3) |
| O(24)-W(2)-O(5) | 96.5(3) | O(22)-W(4)-O(13) | 162.6(3) | W(4)#2-O(6)-W(1) | 138.5(3) |
| O(17)-W(2)-O(5) | 153.3(2) | O(6)#2-W(4)-O(13) | 89.7(2) | W(1)-O(7)-W(6) | 148.4(4) |
| O(25)-W(2)-O(8) | 90.8(3) | O(18)#2-W(4)-O(13) | 85.5(2) | W(5)-O(8)-W(1) | 138.8(3) |
| O(24)-W(2)-O(8) | 163.5(3) | O(21)-W(4)-O(13) | 71.1(2) | W(5)-O(8)-W(2) | 125.6(3) |
| O(17)-W(2)-O(8) | 85.3(2) | O(14)-W(4)-O(13) | 72.7(2) | W(1)-O(8)-W(2) | 94.2(2) |
| O(5)-W(2)-O(8) | 73.3(2) | O(23)-W(5)-O(16) | 104.8(3) | W(6)-O(11)-W(5) | 115.6(3) |
| O(25)-W(2)-O(18) | 165.0(3) | O(23)-W(5)-O(8) | 101.8(3) | W(3)-O(12)-W(6) | 148.3(3) |
| O(24)-W(2)-O(18) | 89.1(3) | O(16)-W(5)-O(8) | 95.0(3) | W(4)-O(13)-W(6) | 95.9(2) |

Continued Table 3

| | | | | | |
|---|---|---|---|---|---|
| O(17)-W(2)-O(18) | 73.4(2) | O(23)-W(5)-O(21) | 98.5(3) | W(4)-O(13)-W(5) | 97.0(2) |
| O(5)-W(2)-O(18) | 86.3(2) | O(16)-W(5)-O(21) | 93.2(3) | W(6)-O(13)-W(5) | 95.5(2) |
| O(8)-W(2)-O(18) | 77.5(2) | O(8)-W(5)-O(21) | 155.3(3) | W(6)-O(14)-W(4) | 114.6(3) |
| O(19)-W(3)-O(20) | 101.7(3) | O(23)-W(5)-O(11) | 93.5(3) | W(5)-O(16)-W(3)#2 | 138.7(3) |
| O(19)-W(3)-O(12) | 99.2(3) | O(16)-W(5)-O(11) | 161.5(2) | W(2)-O(17)-W(3)#2 | 118.1(3) |
| O(20)-W(3)-O(12) | 97.8(3) | O(8)-W(5)-O(11) | 83.2(2) | W(4)#2-O(18)-W(3)#2 | 139.5(3) |
| O(19)-W(3)-O(17)#2 | 97.8(3) | O(21)-W(5)-O(11) | 81.7(2) | W(4)#2-O(18)-W(2) | 125.0(3) |
| O(20)-W(3)-O(17)#2 | 94.5(3) | O(23)-W(5)-O(13) | 163.1(3) | W(3)#2-O(18)-W(2) | 94.1(2) |
| O(12)-W(3)-O(17)#2 | 156.5(3) | O(16)-W(5)-O(13) | 89.2(2) | W(5)-O(21)-W(4) | 119.3(3) |

Symmetry transformations used to generate equivalent atoms: #1: $x$, $-y+1/2$, $z$; #2: $-x+2$, $-y+1$, $-z+1$.

## 2 Results and discussion

Compound **1** was synthesized by dissolving $Na_2WO_4\cdot 2H_2O$ in water by the addition of glycine and $CuCl_2\cdot 2H_2O$. By serious of parallel experiments, it was found that the isolation of the title compound depended on the choices of amino acids and the reaction pH values. The single-crystal structure reveals that compound **1** contains $[H_2W_{12}O_{42}]^{10-}$ anionic clusters decorated by $[Cu(Gly)_2]^{2+}$ subunits, Na cations and lattice water molecules. The $[H_2W_{12}O_{42}]^{10-}$ unit has the well-known paratungstate-B structure[17]. It is centrosymmetric and consists of two types of trimetallic subunits: two $W_3O_{13}$ groups and two $W_3O_{14}$ groups. Each $W_3O_{13}$ group is formed by three edge-sharing $WO_6$ octahedra with a common oxygen atom and three tungsten atoms define a near-equilateral triangle with angles of 59.66°, 59.75° and 60.59°, respectively. In the $W_3O_{14}$ group, three edge-sharing $WO_6$ octahedra are linearly connected and the three tungsten atoms define an open angle with an angle of 116.37°. Two triangular subunits and two open angular ones are held together leaving a central cavity, which contains two disordered protons. The oxygen atoms in the $[H_2W_{12}O_{42}]^{10-}$ unit can be classified into three groups: terminal oxygen atoms with W-O distances between 0.171 8(6)~0.175 8(6) nm; the $\mu_2$-O with W-O distances between 0.177 9(6) ~ 0.221 8(6) nm; the $\mu_3$-O with W-O distances between 0.189 4(6)~0.226 7(6) nm. As expected, the W-O bond distances are in accordance with those in the known paradodecatungstates. The bond valences of oxygen atoms in the polyanion are between 1.6 and 2.1[18], normal for oxygen groups, except that the triply bridging O(13) atom has a sum of 1.2. This indicates that O(13) should be protonated, which is in accordance with the paratungstate-B structure.

More interestingly, in the structure of **1**, each $[H_2W_{12}O_{42}]^{10-}$ ion is decorated by two *cis*-$\{Cu(Gly)_2\}^{2+}$ cations. Such decorated units are then linked further by $Na^+$ ions into a one-dimensional chain (as shown in Fig.1). Crystallographically unique $Cu^{2+}$ is of square pyramid coordination with four ligand atoms from glycines and one oxygen atom from $W_3O_{14}$ subunit. Each glycine molecule, as a bidentate ligand by utilizing its amino and carboxylate groups, chelates to copper in the basal plane, and one terminal oxygen atom of $W_3O_{14}$ occupies the axial position to form the decorated $\{[Cu(Gly)_2]_2[H_2W_{12}O_{42}]\}^{6-}$ anion unit. Moreover,

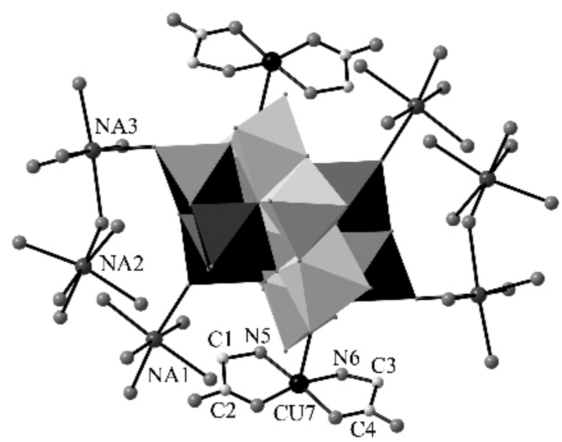


Fig.1 Polyhedral representation of the paradodecatungstate ion $[H_2W_{12}O_{42}]^{10-}$ in **1** acting as a ligand for two $Cu^{2+}$ ions and four $Na^+$ ions; medium gray polyhedra belong to a regular $\{W_3O_{13}\}$ triangular, light gray polyhedra to an open $\{W_3O_{14}\}$ trimeric

such $\{[Cu(Gly)_2]_2[H_2W_{12}O_{42}]\}^{6-}$ unit is covalently linked through two types of $Na^+$ irons to form a one-dimensional chain running parallel to the *b* direction. In another word, it can be seen that each $W_3O_{13}$ offers two terminal oxygen atoms to coordinate to these two types of sodium atoms respectively to offer a distorted octahedral coordination for all sodium atoms. The octahedral geometry around Na(1) atom is completed by four water molecules and two *cis*-oxo groups from two adjacent paratungstate clusters with Na-O distances of 0.236 4(13)~0.245 2(16) nm, while Na(3) atom is completed by four water molecules and two trans-oxo groups from two adjacent paratungstate based decorated units with Na-O distances of 0.235 1(20)~0.257 9(16) nm. It should be pointed out that one of water molecules connected to Na(3) is shared with $Na(2)O_6$ octahedron to form a $Na_2O_{11}$ group. These two types of sodium groups connect the coordinated copper decorated pararungstates into a chain (as shown in Fig.2). Furthermore, of the discrete water molecules, asymmetric O37 and O38 atoms, which located on a usual position and an inversion center respectively, contact with some oxygen atoms of the chain in rather short distance (0.231~0.249 nm). It may be presume that O37 and O38 are all of protonated water molecules, which not only balance the charge of compound **1**, but also increase the stability of the structure by strong hydrogen bonding[19,20]. Some disordered water molecules also make the crystal structure more stable via hydrogen bonding.

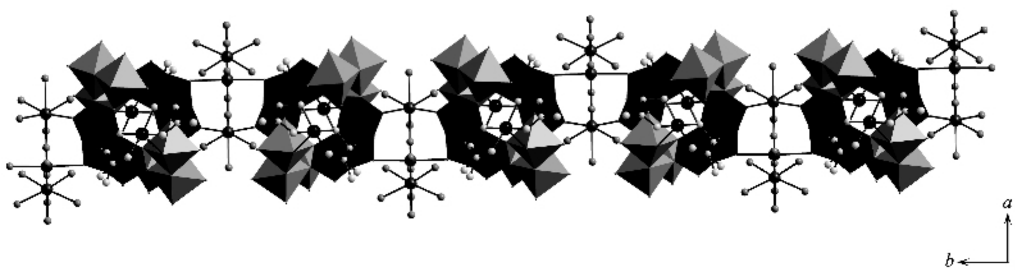


Fig.2 A polyhedral and ball-and-stick representation of the infinite chain in compound **1**

TGA measurement was performed on a NETZSCH STA 449C system. As shown in Fig.3, the weight loss of compound **1** in the ranges 50~250 ℃ (cal. 12.7%, found 12.6%) is in agreement with the removal of the water molecules. The second weight loss between 250 and 530 ℃ is 9.2%, which is in agreement with the removal of the glycine ligands and the weight loss from the $[H_2W_{12}O_{42}]^{10-}$ decomposing to $WO_3$[17].

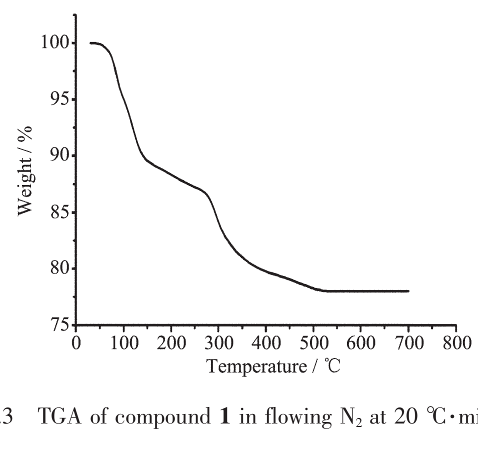


Fig.3 TGA of compound **1** in flowing $N_2$ at 20 ℃·min$^{-1}$

This work confirms the utility of hydrothermal methods for the synthesis of new polymeric materials based on polyoxotungstates decorated by copper-glycine coordination complexes. The successful synthesis of compound **1**, in which each paratungstate cluster was decorated by two $[Cu(Gly)_2]^{2+}$ and linked by sodium ions to form a one-dimensional chain, provides more possibility for designing syntheses of organic-inorganic hybrid materials with amino acid ligands and polyoxotungstates.

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