

基于钒氧多酸与大环铜配合物构筑的三维配位聚合物的合成与表征

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摘要: 通过 $[\text{CuL}](\text{ClO}_4)_2$ ($\text{L}=5,12$ -二甲基-1,8-二乙醇基-1,3,6,8,10,13-六氮杂环十四烷)与 NH_4VO_3 反应,得到一个钒氧多酸桥联大环铜配合物的三维配位聚合物 $\{[\text{CuL}][\text{VO}_3]_2 \cdot 0.67\text{H}_2\text{O}\}_n$ 。并对其进行了元素分析、红外光谱、紫外光谱、热重和 X-射线单晶衍射测定。单晶结构测试结果表明配合物属于三方晶系, $R\bar{3}$ 空间群。在晶体结构中,铜原子与大环配体上的 4 个氮原子和钒氧四面体 $[\text{VO}_4]$ 中的 2 个氧原子配位,形成畸变的八面体构型。钒氧多酸阴离子 $[\text{V}_6\text{O}_{18}]^{6-}$ 桥联大环配合物 $[\text{CuL}]^{2+}$ 形成一个具有一维通道的三维配位聚合物。

关键词: 大环铜配合物; 钒氧多酸; 晶体结构

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Synthesis and Structure of a Three-Dimensional Polyoxovanadate-Bridged Macrocyclic Copper Complex

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Abstract: A three-dimensional transition metal copper macrocyclic complex $\{[\text{CuL}][\text{VO}_3]_2 \cdot 0.67\text{H}_2\text{O}\}_n$ ($\text{L}=5,12$ -dimethyl-1,8-dihydroxyethyl-1,3,6,8,10,13-hexaazacyclotetradecane) has been isolated from the reactions of $[\text{CuL}](\text{ClO}_4)_2$ with NH_4VO_3 , and structurally characterized by elemental analysis, IR, TG, UV spectrum and X-ray diffraction. The title compound crystallizes in the trigonal system, space group $R\bar{3}$ with $a=1.687\ 7\ (12)\ \text{nm}$, $b=1.687\ 7(12)\ \text{nm}$, $c=2.163\ 0(3)\ \text{nm}$, $M_r=591.90$, $V=5.335\ 4(10)\ \text{nm}^3$, $Z=9$, $D_c=1.654\ \text{g}\cdot\text{cm}^{-3}$, $F(000)=2\ 739$, $\mu=1.714\ \text{mm}^{-1}$, the final $R=0.047\ 0$ and $wR=0.134\ 7$. The Cu(II) atom lies on an inversion center and is octahedrally coordinated by four nitrogen atoms of the tetradentate macrocyclic L ligand in the equatorial plane and two oxygen atoms of $[\text{VO}_4]$ tetrahedrons in axial positions. The title compound shows a three-dimensional structure, which is constructed by the links of hexanuclear $[\text{V}_6\text{O}_{18}]^{6-}$ rings with $[\text{CuL}]^{2+}$, forming one-dimensional channels occupied by guest water molecules. CCDC: 902742.

Key words: macrocyclic copper complex; polyoxovanadate; crystal structure

Recently, the assembly of vanadium polyoxoanion clusters with transition metal complexes became the focus of chemists, and many extended structures have

been reported using transition metal complexes and polyoxovanadate clusters as building blocks^[1-12].

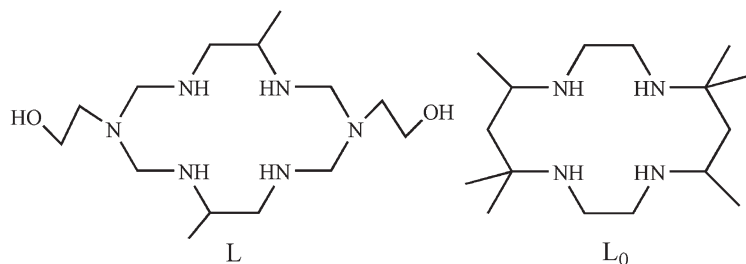
In our previous report^[9], two different three-

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dimensional structures of $[\text{NiL}_0][\text{VO}_3] \cdot 0.33\text{H}_2\text{O}$ and $[\text{CuL}_0][\text{VO}_3]_2 \cdot 0.33\text{H}_2\text{O}$ ($\text{L}_0=5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradecane, Scheme 1) were obtained by the reactions of $[\text{ML}_0](\text{ClO}_4)_2$ ($\text{M}=\text{Ni}, \text{Cu}$) with NH_4VO_3 under same conditions. Compounds $[\text{NiL}_0][\text{VO}_3]_2 \cdot 0.33\text{H}_2\text{O}$ and $[\text{CuL}_0][\text{VO}_3]_2 \cdot 0.33\text{H}_2\text{O}$ display three-dimensional structures, which are constructed through the connections of $[\text{V}_6\text{O}_{18}]^{6-}$ rings with $[\text{NiL}_0]^{2+}$, and $[\text{VO}_3]_n^{n-}$ chains with $[\text{CuL}_0]^{2+}$, respectively. As a continuance of our research on the constructions of functional coordination polymers, a three-dimensional complex was obtained when $[\text{CuL}](\text{ClO}_4)_2$ ($\text{L}=5,12$ -dimethyl-1,8-dihydroxyethyl-1,3,6,8,10,13-hexaazacyclotetradecane) were reacted with NH_4VO_3 under the same condition. It is interesting to note that the three-dimensional structure was changed from $[\text{VO}_3]_n^{n-}$ chain in $[\text{CuL}_0][\text{VO}_3]_2 \cdot 0.33\text{H}_2\text{O}$ to $[\text{V}_6\text{O}_{18}]^{6-}$ ring in the title compound, indicating the macrocyclic ligand can affect the three-dimensional structures. Herein, we report on the preparation and structure of the title compound. The title compound displays a three-dimensional structure, which is constructed



Scheme 1 Macrocylic ligands L and L_0

1.2 Synthesis of $[\text{CuL}][\text{VO}_3]_2 \cdot 0.67\text{H}_2\text{O}$

An aqueous solution (20 mL) of NH_4VO_3 (0.117 g, 1 mmol) was layered with an acetonitrile solution (20 mL) of $\text{CuL}(\text{ClO}_4)_2$ (0.181 g, 0.33 mmol). Several weeks later, red block-shaped crystals were obtained in ~25% yield (based on V). Anal. Calcd. (%) for $\text{C}_{14}\text{H}_{35.33}\text{N}_6\text{CuO}_{8.67}\text{V}_2$: C, 28.40; H, 6.01; N, 14.20; Cu, 10.74; V, 17.21. Found (%): C, 28.2; H, 5.9; N, 14.0; Cu, 10.45; V, 16.89. IR (KBr, cm^{-1}): 3 381m, 3 167m, 2 874w, 1 622s, 1 431s, 1 395m, 1 290w, 1 238w, 1 100w, 1005vs, 893w, 729m.

1.3 Crystal structure determination

A single crystal of the title compound with

through the connections of $[\text{V}_6\text{O}_{18}]^{6-}$ rings with $[\text{CuL}]^{2+}$, generating one-dimensional channels.

1 Experimental

1.1 Materials and general methods

The macrocyclic ligand (L) and its Cu(II) complex was prepared according to the literature method^[13-16]. All the other chemicals were commercially sourced and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. Cu and V were determined by a TJA IRIS (HR) inductively coupled plasma-atomic emission spectrometer (ICP). IR spectra were recorded in the 4 000~400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. UV spectra were recorded in the 200~400 nm region on a UV8200 spectrometer. TG analyses were performed on a Perkin-Elmer TGS-2 instrument in flowing air with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. XRD data were recorded in a Bruker D8 ADVANCE X-ray powder diffractometer (Cu $K\alpha$, $\lambda=0.154\ 18\ \text{nm}$).

dimensions of 0.36 mm \times 0.32 mm \times 0.15 mm, was mounted on a glass fiber for data collection which was performed on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 173 (2) K. A total of 9 076 reflections were collected in the range of $1.68^{\circ} < \theta < 27.03^{\circ}$, of which 2 599 were independent ($R_{\text{int}}=0.023\ 0$) and 2 112 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. Empirical absorption correction was applied by using the SADABS program^[17]. The structure was solved by direct methods yielding the positions of all non-hydrogen atoms which were first refined

isotropically and then anisotropically. All hydrogen atoms (except those of nitrogen atoms and water molecules) were placed in the calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final cycle of full-matrix least-squares refinement. The hydrogen atoms of the macrocyclic nitrogen atoms were located in the difference Fourier map and refined isotropically, and the hydrogen atoms of water molecule in the title compound were not added as they were located in a special position. All calculations were performed using the SHELXTL

system of computer programs^[18]. N3, C5, C6 and O4 atoms are disordered over two symmetry related sites in a 9:11 ratio, and the hydrogen atoms connected to disordered N3 atoms were placed in calculated positions with fixed isotropic thermal parameters. The final $R=0.047\ 0$, and $wR=0.134\ 7$ for 2 112 observed reflections with $I>2\sigma(I)$, and $R=0.059\ 2$ and $wR=0.145\ 8$ for 259 9 independent reflections. $S=1.048$, $(\Delta/\sigma)_{\max}=0.000$, $(\Delta\rho)_{\max}=1400$ and $(\Delta\rho)_{\min}=-952\ \text{e}\cdot\text{nm}^{-3}$. The selected bond lengths and bond angles are listed in Table 1.

CCDC: 902742.

Table 1 Selected bond distances (nm) and angles ($^{\circ}$)

Cu(1)-N(1)	0.203 4(4)	Cu(1)-N(2)	0.200 0(3)	Cu(1)-O(1)	0.238 0(3)
V(1)-O(1)	0.163 4(3)	V(1)-O(2)	0.164 1(3)	V(1)-O(3)	0.180 6(3)
V(1)-O(3) ^B	0.178 7(3)				
N(2)-Cu(1)-O(1)	90.07(13)	O(2)-V(1)-O(3)	110.63(17)	N(2)-Cu(1)-N(1)	94.05(15)
N(2)-Cu(1)-O(1) ^A	89.93(13)	O(2)-V(1)-O(3) ^B	108.98(16)	N(2)-Cu(1)-N(1) ^A	85.95(15)
N(1)-Cu(1)-O(1)	86.60(12)	O(1)-V(1)-O(2)	108.00(17)	O(1)-V(1)-O(3) ^B	109.46(15)
N(1)-Cu(1)-O(1) ^A	93.40(12)	O(1)-V(1)-O(3)	108.63(15)		

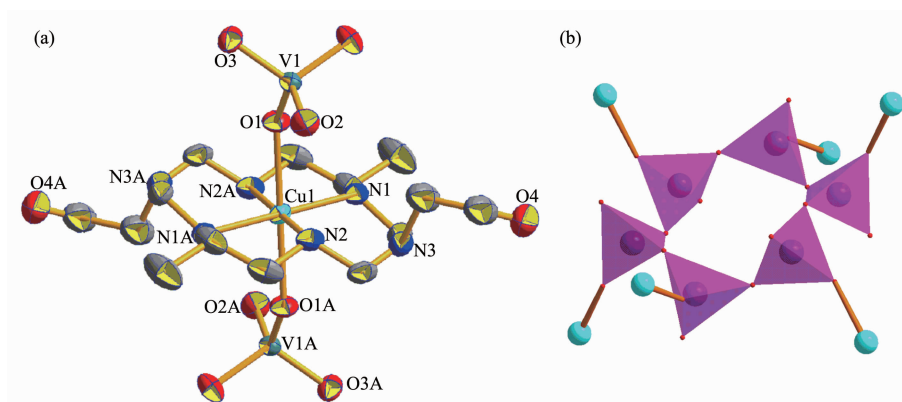
Symmetry codes: A: $2/3-x$, $1/3-y$, $1/3-z$; B: y , $-x+y$, $-z$

2 Results and discussion

2.1 Description of the crystal structure

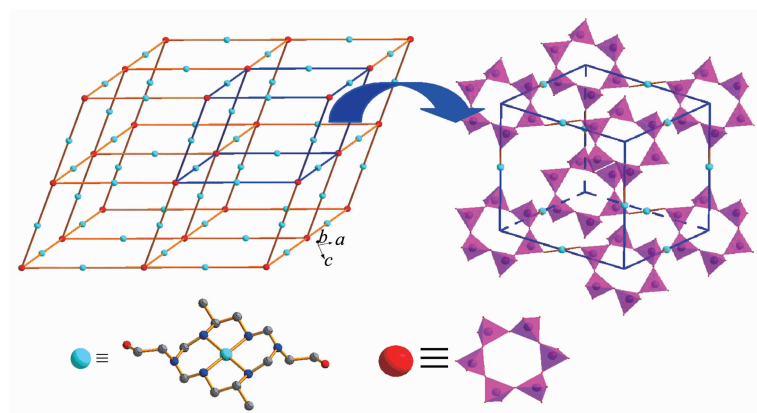
X-ray crystal structural analysis reveals that the asymmetry unit of compound contains one $[\text{CuL}]^{2+}$ cation, two $[\text{VO}_3]^-$ anions and two-third of water molecules (Fig.1). Each Cu (II) atom lies on an inversion center, and is coordinated with four macrocyclic nitrogen atoms in the equatorial plane and two oxygen atoms of two $[\text{VO}_4]$ tetrahedrons in axial positions. The Cu-N distances (0.200 0(3)~0.203 4(4) nm) are shorter than the Cu-O distances (0.238 0(3) nm), reflecting Jahn-Teller distortion. The vanadium center in $[\text{VO}_4]$ tetrahedron is coordinated with two bridging oxygen atoms (O_b) and two terminal oxygen atoms (O_t), the V- O_b bond distances (0.178 7(3) and 0.180 6(3) nm) are longer than the V- O_t distance (0.163 4(3) and 0.164 1(3) nm) (Table 1). Based on valence sum calculations^[19] ($S=\exp[(1.799-r)/0.37]$, $r=\text{V-O distance}$), the value for the V atom is 5.11,

indicating that the V atom is in the +5 oxidation state. In our previous reported^[9], we found the complex $[\text{CuL}_0][\text{VO}_3]_2$ displays a three-dimensional structure, which is constructed through the connections of $[\text{VO}_3]_n^-$ chains with $[\text{CuL}_0]^{2+}$. However, six $[\text{VO}_4]$ tetrahedrons form a hexanuclear $[\text{V}_6\text{O}_{18}]^{6-}$ ring through sharing six μ_2 -oxygen atoms, and a three-dimensional porous coordination polymer is formed through the connecting of μ_6 - $[\text{V}_6\text{O}_{18}]^{6-}$ with $[\text{CuL}]^{2+}$ in $[\text{CuL}][\text{VO}_3]_2$ (Fig.2, Fig.3). The building unit of $[\text{VO}_3]^-$ in $[\text{CuL}_0][\text{VO}_3]_2$ transformed to $[\text{V}_6\text{O}_{18}]^{6-}$ in $[\text{CuL}][\text{VO}_3]_2$ may due to the steric hindrance of macrocyclic ligand L. Each $[\text{V}_6\text{O}_{18}]^{6-}$ ring is coordinated with six $[\text{CuL}]^{2+}$, in which three $[\text{CuL}]^{2+}$ locate above the ring, and the other three $[\text{CuL}]^{2+}$ locate below the ring (Fig.1). The pore size is 0.44 nm×0.44 nm along the c axis. The pores are filled with guest water molecules, and the solvent accessible volume of the title compound was estimated by PLATON^[20] to be 3.9% (0.2066 nm³) of the total crystal volume.



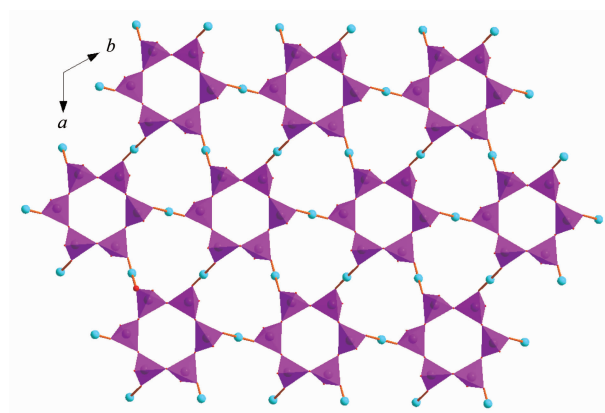
(a) H atoms and water molecule are omitted for clarity; the symmetry codes for the generated atoms: A ($2/3-x, 1/3-y, 1/3-z$).

Fig.1 (a) ORTEP diagram of the asymmetry unit of compound with 50% probability displacement ellipsoids;
(b) The hexanuclear $[\text{V}_6\text{O}_{18}]^{6-}$ ring through sharing six μ_2 -oxygen atoms



$[\text{V}_6\text{O}_{18}]^{6-}$ ring as red ball, $[\text{CuL}]^{2+}$ as turquoise ball.

Fig.2 Skeleton drawing of the title compound



Macrocyclic ligand L and the guest water molecules are omitted for clarity

Fig.3 3D framework with 1D hexagonal channels along the c axis

2.2 IR spectra

In the IR spectra of the title compound, the middle absorption bands at about $3\,381\text{ cm}^{-1}$ are

assigned to the stretching vibration of the hydroxy groups. The middle absorption bands at about $3\,167\text{ cm}^{-1}$ are assigned to the N-H stretching vibration. The

characteristic bands at $1\,005\text{ cm}^{-1}$ attributed to the V-O group, in the region of $893\sim729\text{ cm}^{-1}$ due to the bridging V-O-V group^[21-22] and in the region $1\,622\sim1\,395\text{ cm}^{-1}$ assigned to the C-C and C-N stretching vibrations of the organic amines^[23].

2.3 XRD and TG analysis

The simulated and experimental XRD patterns of the title compound are shown in Fig.4. Their peak positions are in good agreement with each other, indicating the phase purity of the products. The thermogravimetric analyses were carried out in flowing air with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in the temperature range $25\sim800\text{ }^{\circ}\text{C}$, as shown in Fig.5. The TG curves shows that the observed weight loss (2.3%) is consistent with the calculated value (2.1%) below $250\text{ }^{\circ}\text{C}$. The framework is stable up to about $200\text{ }^{\circ}\text{C}$, and then began to decompose upon further heating.

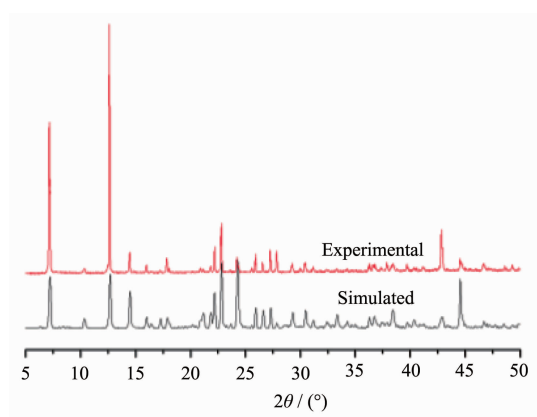


Fig.4 XRD pattern of the title compound

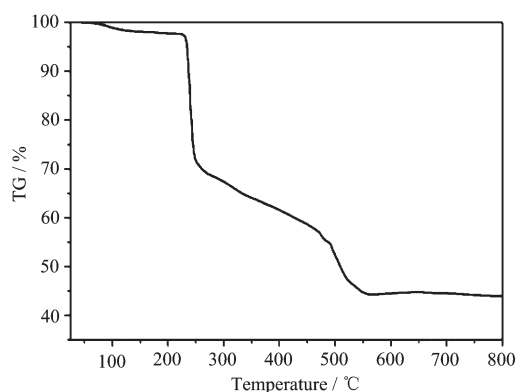


Fig.5 TG curve of the title compound

2.4 Electronic spectra

The UV spectra of the title compound have been investigated in $1\text{ mol}\cdot\text{L}^{-1}\text{ H}_2\text{SO}_4$ solution (Fig.6). The

title compound displays one absorption band at about 222 nm , which should be assigned to the $\pi\text{-}\pi^*$ transition of macrocyclic ligand^[24-25].

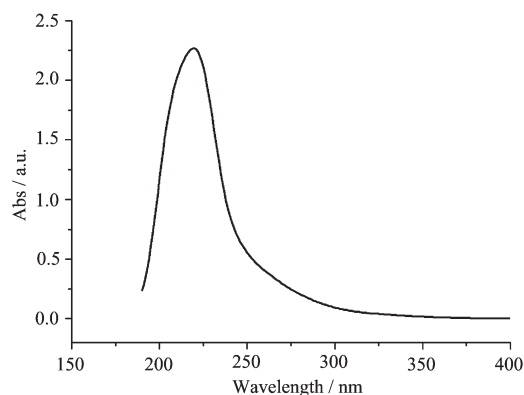


Fig.6 UV spectra of the title compound

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