

## 两个含吡啶取代苯酚配体的铜配合物的合成与晶体结构

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**摘要:** 以 2-[*N,N*-二(2-吡啶甲基)氨基甲基]-6-醛基-4-甲基苯酚(L)为配体, 合成了 2 个单核铜配合物[CuL(CH<sub>3</sub>CN)(ClO<sub>4</sub>)]ClO<sub>4</sub>(**1**)和 *cis*-[CuL(NCS)<sub>2</sub>]·0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>(**2**), 对它们进行了紫外、红外、质谱、元素分析和单晶结构表征。2 个配合物都属于单斜晶系, 每个铜均为扭曲的八面体构型。作为四齿配体, L 通过 2 个吡啶氮原子, 1 个叔胺氮原子和 1 个酚氧原子和铜离子配位。在配合物 **1** 中, 乙腈和 1 个 ClO<sub>4</sub><sup>-</sup>参与配位, 而在配合物 **2** 中 2 个硫氰根离子为顺式配位。

**关键词:** 苯酚配体; 铜配合物; 晶体结构

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## Syntheses and Crystal Structures of Two Copper Complexes with Pyridyl-Substituted Phenol Ligand

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**Abstract:** Two mononuclear copper(II) complexes, [CuL(CH<sub>3</sub>CN)(ClO<sub>4</sub>)]ClO<sub>4</sub>(**1**) and *cis*-[CuL(NCS)<sub>2</sub>]·0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>(**2**) (L=2-[*N,N*-di (2-pyridylmethyl)aminomethyl]-6-aldehydo-4-methylphenol) have been synthesized and characterized by UV-Vis, FTIR, ESI-MS, elemental analysis and single crystal X-ray crystallography. Both **1** and **2** crystallize in a monoclinic system. Each copper(II) ion locates in a distorted octahedron geometry. As a tetradentate chelating ligand, the L coordinates to copper(II) ion via two pyridyl N atoms, one N atom of tertiary amine, and one phenol O atom. In **1**, an acetonitrile molecule and a perchlorate anion also take part in coordination; while there are two *cis*-disposed NCS<sup>-</sup> ions in **2**. CCDC: 938954, **1**; 938955, **2**.

**Key words:** phenol ligand; Cu(II) complex; crystal structure

A ligand including two adjacent but dissimilar coordination sites has been collectively termed as “compartmental ligand”. The possible application of this type of ligand is to mimic the dimetallic biosites and catalysis associated with some native enzyme<sup>[1-10]</sup>. Over the past two decades, a large number of such ligand have been designed and investigated<sup>[1-6]</sup>. Among them, phenol-based compartmental ligands are one of

the most notable systems. In the process of synthesis of the phenol-based compartmental ligands, 2-[*N,N*-di (2-pyridylmethyl)aminomethyl]-6-aldehydo-4-methylphenol (L) often acts as an important intermediate<sup>[11-15]</sup>. Its crystal structure has been recently reported by us<sup>[16]</sup> and its dinuclear Mn(II) complex [Mn<sub>2</sub>L<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub> was also obtained by our group in 2007<sup>[17]</sup>. As a continuation of our investigation on the L ligand and

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its complex, herein we present the syntheses, crystal structures and spectral characterization of two mononuclear copper (II) complexes with L ligands,  $[\text{CuL}(\text{CH}_3\text{CN})(\text{ClO}_4)]\text{ClO}_4$  (**1**) and  $\text{cis-}[\text{CuL}(\text{NCS})_2] \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (**2**).

## 1 Experimental

### 1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand L was prepared according to the literature method<sup>[16]</sup> and its structure is shown in Scheme 1. Elemental analyses (C, H, N, S) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectrum was recorded on a Nicolet Avatar 380 FTIR instrument with KBr pellets in the range of  $4000 \sim 400 \text{ cm}^{-1}$ . UV-Vis spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer at room temperature in methanol solution. Electrospray ionization mass spectrum (ESI-MS) was recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was  $0.2 \text{ cm}^3 \cdot \text{min}^{-1}$ . The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40 V, and  $260^\circ\text{C}$ , respectively.

### 1.2 Synthesis of complexes 1 and 2

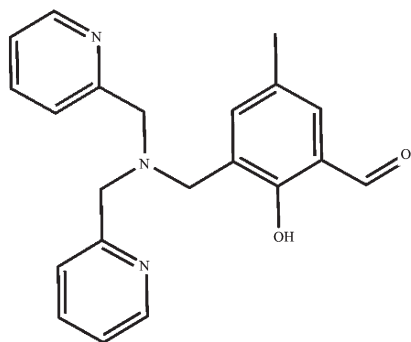
$[\text{CuL}(\text{CH}_3\text{CN})(\text{ClO}_4)]\text{ClO}_4$  (**1**): A solution of Cu  $(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol) in THF (1.0 mL) was added dropwise to a solution of L (0.1 mmol) in THF (1.0 mL). The mixture was stirred at room temperature for 12 h. The resulting blue precipitate was separated by centrifugation, then washed with THF and dried under vacuum to give the product (yield: 86.2%). THF vapor

diffusion to the solution of the complex in acetonitrile afforded blue crystals of **1** suitable for X-ray crystallographic analysis. Elemental analyses calcd. for  $\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{CuN}_4\text{O}_{10}$  (%): C 42.44, H 3.72, N 8.61; found (%): C 42.26, H 3.50, N 8.42. UV ( $\text{CH}_3\text{OH}$ , nm):  $\lambda=281$  (1.73), 336 (1.21). IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3 447 (b, s); 2 932 (w); 2 072 (s); 1 655 (s); 1 611 (s); 1120 (vs); 928 (w); 627 (s). ESI-MS:  $m/z=525.0, 483.4, 459.6$ .

$\text{cis-}[\text{CuL}(\text{NCS})_2] \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (**2**): A solution of Cu  $(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol) in THF (1.0 mL) was added dropwise to a solution of L (0.1 mmol) and  $\text{NH}_4\text{SCN}$  (0.1 mmol) in THF (1.0 mL). The mixture was stirred at room temperature for 12 h, blue-green precipitate was formed and separated by centrifugation, then washed with THF and dried under vacuum to give the product (yield: 72.3%). Diffusion of dioxane to the solution of the complex in acetonitrile afforded blue-green crystals of **2** suitable for X-ray crystallographic analysis. Elemental analyses calcd. for  $\text{C}_{25}\text{H}_{25}\text{CuN}_5\text{O}_3\text{S}_2$  (%): C 52.57, H 4.41, N 12.26, S 11.23; found (%): C 52.38, H 4.25, N 12.02, S 11.06. UV ( $\text{CH}_3\text{OH}$ , nm):  $\lambda=279$  (1.47), 338 (1.02). IR data ( $\nu$ ,  $\text{cm}^{-1}$ ): 3 441 (b, s); 2 909(w); 2 852 (w); 2 089 (vs); 2 061 (vs); 1 665 (s); 1 608 (s). ESI-MS:  $m/z=482.5$ .

### 1.3 Crystal structure determination

The well-shaped single crystals of **1** and **2** were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo  $K\alpha$  ( $\lambda=0.071\ 073$  nm) radiation. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least squares procedures using SHELXTL software<sup>[18]</sup>. All non-hydrogen atoms were anisotropically refined. All H atoms were located from a difference map and refined isotropically. In **2**, atoms S1, S1A and S1B of one  $\text{SCN}^-$  anion were found to be highly disordered with an occupancy factor of 0.50, 0.25 and 0.25, respectively, and atoms S2 and N5 of another  $\text{SCN}^-$  anion were also highly disordered, with an occupancy factor of 0.884(4) for S2 and N5 and 0.116(4) for S2A and N5A. Atoms O3 and O3A of dioxane were disordered over two positions and fixed at 0.50. Crystallographic data for **1**



Scheme 1 Structure of L ligand

and **2** are summarized in Table 1. Selected bond distances and angles are given in Table 2.

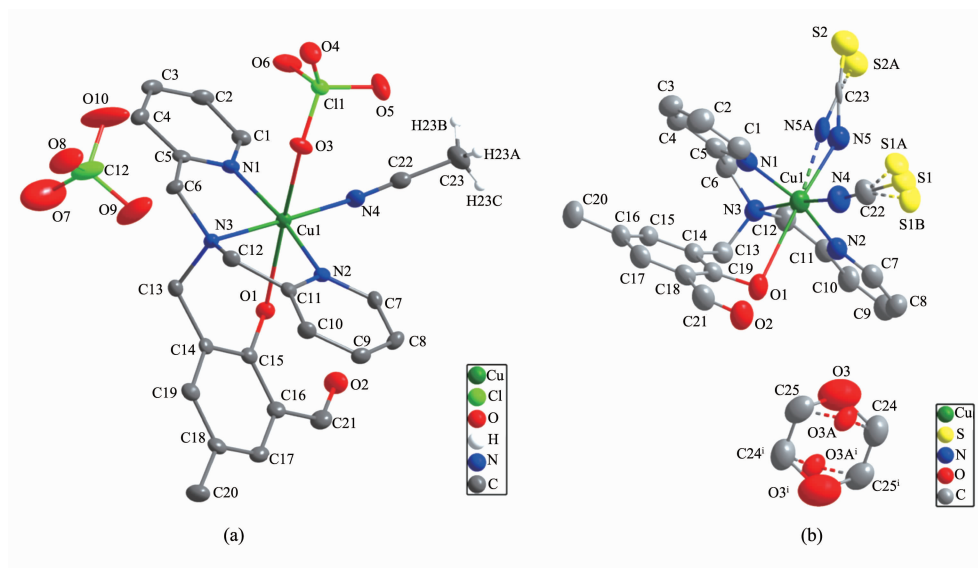
CCDC: 938954, **1**; 938955, **2**.

## 2 Results and discussion

### 2.1 Structure description of **1**

A projection of the structure of **1** is presented in Fig.1a together with the atomic labeling system. The complex crystallizes in the monoclinic space group  $P2_1/n$  and the asymmetric unit consists of one Cu(II) cation, one L ligand, an acetonitrile molecule and two perchlorate anions. The Cu1 atom is coordinated by four nitrogen atoms (three from L ligand and one from acetonitrile) in the equatorial plane and two oxygen atoms (one from phenol and another from perchlorate) in the axial positions to form a distorted  $[CuN_4O_2]$  octahedron. The L ligand adopts a tetradentate coordination mode via two pyridyl N atoms, one N atom of tertiary amine and one phenol O atom. This

feature is similar to those found in two reported mononuclear complexes  $[CuLBr_2] \cdot 0.5H_2O$  and  $[MnLCl_2]^{[19]}$ . Notably, the aldehyde group of the L ligand does not take part in coordination, while the phenol group remains protonated though it behaves as an axial donor. The bond lengths of Cu1-N within the plane are from 0.1974(3) to 0.2020(3) nm, which are in the normal ranges observed for the related Cu(II) complex<sup>[19]</sup>. However, the bond distances of Cu1-O are much shorter than that found in  $[CuLBr_2] \cdot 0.5H_2O$ <sup>[19]</sup>. The phenol ring makes dihedral angles of  $29.6^\circ$  and  $30.5^\circ$  with the pyridyl ring with N1 and N2, respectively. The dihedral angle between two pyridyl rings is  $2.6^\circ$ . All these values are smaller than those observed in free L ligand<sup>[16]</sup>. The crystal structure of **1** is further stabilized by one kind of strong intramolecular O1–H1B  $\cdots$  O2 hydrogen bond and five kinds of intermolecular C–H $\cdots$ O hydrogen bonds (Table 3 and Fig.2a).



All hydrogen atoms except  $CH_3CN$  are omitted for clarity; Symmetry code: **2**:  $i - x, 1 - y, 2 - z$

Fig.1 Projection of structures of **1** (a) and **2** (b) with 40% thermal ellipsoids probability

Table 1 Crystal data and structure refinement for **1** and **2**

Complexes	<b>1</b>	<b>2</b>
Empirical formula	$C_{23}H_{24}Cl_2CuN_4O_{10}$	$C_{25}H_{25}CuN_5O_3S_2$
Formula weight	650.90	571.16
Crystal size/mm	0.20×0.16×0.14	0.14×0.12×0.08
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$

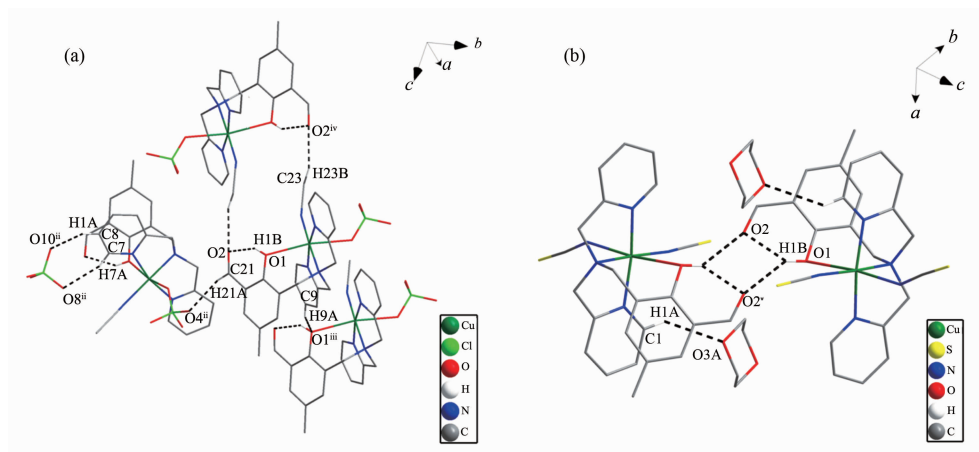
Continued Table 1

$a / \text{nm}$	0.827 82(16)	0.907 73(9)
$b / \text{nm}$	2.111 9(4)	1.125 75(11)
$c / \text{nm}$	1.500 4(3)	2.517 2(2)
$\alpha / (^{\circ})$	90.044(3)	91.938 0(10)
$V / \text{nm}^3$	2.623 1(9)	2.570 8(4)
$Z$	4	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.648	1.476
$F(000)$	1 332	1180
$\mu / \text{mm}^{-1}$	1.101	1.049
$\theta$ Range/ $(^{\circ})$	1.66~25.00	1.98~25.00
Reflections collected	18 295	17 433
Independent reflections	4611 ( $R_{\text{int}}=0.0671$ )	4483 ( $R_{\text{int}}=0.036 0$ )
Reflections observed ( $I > 2\sigma(I)$ )	3 533	3 324
Data/restraints/parameters	5 955/138/434	4 483/59/371
Goodness-of-fit on $F^2$	1.060	1.049
$R/wR$ ( $I > 2\sigma(I)$ )	0.049 3/0.112 5	0.063 9/0.183 2
$R/wR$ (all data)	0.068 3/0.117 9	0.085 6/0.197 4
$(\Delta\rho)_{\text{max}} (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	462, -544	1 311, -640

## 2.2 Structure description of 2

The single crystal structure analysis reveals that **2** crystallizes in the monoclinic space group  $P2_1/c$  (Fig.1b). The asymmetric unit consists of one Cu(II) cation, one L ligand, two  $\text{NCS}^-$  anions and 0.5 dioxane molecule. The Cu1 atom in **2** is coordinated by four nitrogen atoms (three from L ligand and one from  $\text{NCS}^-$ ) in the equatorial plane and one phenol oxygen atom and another  $\text{NCS}^-$  in the axial positions to form a distorted  $[\text{CuN}_5\text{O}]$  octahedron. Similar to **1**, the L

ligand remains a tetradentate chelating agent and the aldehyde group does not coordinate. Notably, two coordinated  $\text{NCS}^-$  ions locate in a *cis*-arrangement in **2** and the  $\text{NCS}^-$  ions are almost linear. The bond lengths of Cu1-N within the plane are from 0.194 1(5) to 0.203 3 (4) nm. The distance of Cu1-N (CS) in the axial position is 0.044 3 nm longer than that in the equatorial plane<sup>[20]</sup>. The bond distance of Cu1-O1 in **2** is 0.031 nm longer than that in **1**, showing the phenol O atom in **2** is a weaker donor. The phenol ring



Symmetry codes: **1**:  $^{\text{ii}} 0.5-x, y-0.5, 0.5-z$ ;  $^{\text{iii}} 1+x, y, z$ ;  $^{\text{iv}} -x, -y, -z$ ; **2**:  $^{\text{v}} 1-x, 1-y, 2-z$

Fig.2 Hydrogen bonding interactions in **1** (a) and **2** (b)

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

<b>1</b>					
Cu1-N2	0.197 4(3)	Cu1-O1	0.256 7(3)	Cl1-O3	0.144 7(3)
Cu1-N1	0.1976(3)	Cu1-O3	0.248 0(3)	N4-C22	0.113 5(6)
Cu1-N3	0.202 0(3)	C15-O1	0.137 0(5)		
Cu1-N4	0.197 8(4)	C21-O2	0.123 2(6)		
N2-Cu1-N1	166.91(15)	N1-Cu1-N3	83.43(14)	O1-Cu1-N2	84.97(11)
N2-Cu1-N4	95.40(14)	N4-Cu1-N3	177.72(15)	O3-Cu1-N2	85.62(12)
N1-Cu1-N4	97.07(15)	O1-Cu1-O3	169.41(10)	N4-C22-C23	178.9(5)
N2-Cu1-N3	83.95(14)	O1-Cu1-N1	98.10(11)	Cu1-O3-Cl1	125.3(5)
<b>2</b>					
Cu1-N2	0.199 6(4)	Cu1-O1	0.287 7(5)	N5-C23	0.130 1(7)
Cu1-N1	0.200 6(4)	Cu1-N5	0.238 4(6)	N4-C22	0.112 3(7)
Cu1-N3	0.203 3(4)	C19-O1	0.135 7(6)		
Cu1-N4	0.194 1(5)	C21-O2	0.120 5(7)		
N2-Cu1-N1	163.04(17)	N1-Cu1-N3	81.95(16)	O1-Cu1-N3	84.46(11)
N2-Cu1-N4	98.1(2)	N4-Cu1-N3	173.17(17)	O1-Cu1-N5	172.32(51)
N1-Cu1-N4	97.46(18)	O1-Cu1-N1	93.22(41)	N4-C22-S1	179.6(7)
N2-Cu1-N3	81.78(16)	O1-Cu1-N2	80.49(71)	N5-C23-S2	172.9(4)

**Table 3** Hydrogen bonding interactions in **1** and **2**

<b>1</b>				
D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠ DHA / (°)
O1-H1B...O2	0.082	0.186	0.2583(5)	147
C7-H7A...O8 <sup>ii</sup>	0.093	0.246	0.3336(6)	158
C8-H8A...O10 <sup>iii</sup>	0.093	0.256	0.3168(6)	124
C9-H9A...O1 <sup>iii</sup>	0.093	0.247	0.3300(5)	149
C21-H21A...O4 <sup>ii</sup>	0.093	0.244	0.3306(5)	155
C23-H23B...O2 <sup>iv</sup>	0.096	0.259	0.3322(6)	133
<b>2</b>				
O1-H1B...O2	0.082	0.198	0.2687(5)	143
O1-H1B...O2 <sup>v</sup>	0.082	0.247	0.3136(6)	139
C1-H1A...O3A <sup>v</sup>	0.093	0.256	0.3156(5)	122

Symmetry codes: **1**: <sup>ii</sup> 0.5-x, y-0.5, 0.5-z; <sup>iii</sup> 1+x, y, z; <sup>iv</sup> -x, -y, -z; **2**: <sup>v</sup> 1-x, 1-y, 2-z

makes dihedral angles of 27.5° and 33.4° with the pyridyl ring with N1 and N2, respectively. The dihedral angle between two pyridyl rings is 8.1°. These values are slightly different from those observed in **1**. Similar to **1**, there is also one kind of strong intramolecular O1-H1B...O2 hydrogen bond in **2**. Moreover, one kind of strong intermolecular O1-H1B...O2<sup>v</sup> hydrogen bond connects two molecules of **2** to form a dimer which is further stabilized by one kind of intermolecular C1-H1A...O3A<sup>v</sup> hydrogen bond

between the pyridyl ring with N1 and the dioxane (Fig.2b and Table 3).

### 2.3 Spectral characterization

In the IR spectrum of the complex **1** (or **2**), a broad band at 3 447 (or 3 441) (s) cm<sup>-1</sup> can be assigned to the O-H stretching vibration of phenol. A strong band at 1 655 (or 1 665) cm<sup>-1</sup> is attributed to the C=O stretching vibration of the aldehyde group. A band at 1 611 (or 1 608) (s) cm<sup>-1</sup> can be assigned to the coordinated pyridine ring [21]. In **1**, three bands at

1 120 (vs), 928 (w) and 627 (s)  $\text{cm}^{-1}$  are attributable to the IR-allowed  $\nu$  mode, IR-forbidden  $\nu$  mode and the non-degenerate  $\text{ClO}_3^-$  symmetrical bending frequency of the  $\text{ClO}_4^-$  anions, respectively<sup>[22]</sup>; a strong band at 2 072  $\text{cm}^{-1}$  is assigned to the  $\text{C} \equiv \text{N}$  stretching vibration of acetonitrile. In **2**, two very strong bands at 2 089 and 2 061  $\text{cm}^{-1}$  are attributed to the  $\text{C} \equiv \text{N}$  stretching vibrations of two thiocyanate groups, revealing that two  $\text{NCS}^-$  anions are in a *cis*-arrangement<sup>[21,23]</sup>. These features are in agreement with the results of X-ray analysis.

The structures of **1** and **2** in methanol solution were also studied by electrospray ionization mass

spectrometry (ESI-MS). Fig.3a displays the positive ESI mass spectrum of **1** and three peaks are observed. The peak at  $m/z$  525.0 is  $[\text{Cu}_2\text{L}_2(\text{ClO}_4)_2(\text{CH}_3\text{OH})]^{2+}$  ion. Two peaks at  $m/z$  483.4 and 459.6 are  $[\text{Cu}(\text{L-H})(\text{CH}_3\text{CN})(\text{CH}_3\text{OH})]^+$  and  $[\text{Cu}_2(\text{L-H})_2(\text{CH}_3\text{OH})_3]^{2+}$  ion, respectively. The positive ESI mass spectrum of **2** is shown in Fig.3b and a peak at  $m/z$  482.5 is  $[\text{CuL}(\text{NCS})]^+$  ion.

The UV-Vis spectra of **1** and **2** in methanol solution are similar. The intense band at 281 (279) nm is attributed to the  $\pi-\pi^*$  transition of the aromatic rings. One band at 336 (338) nm corresponds to the  $d-d$  transition of  $\text{Cu(II)}$  ion.

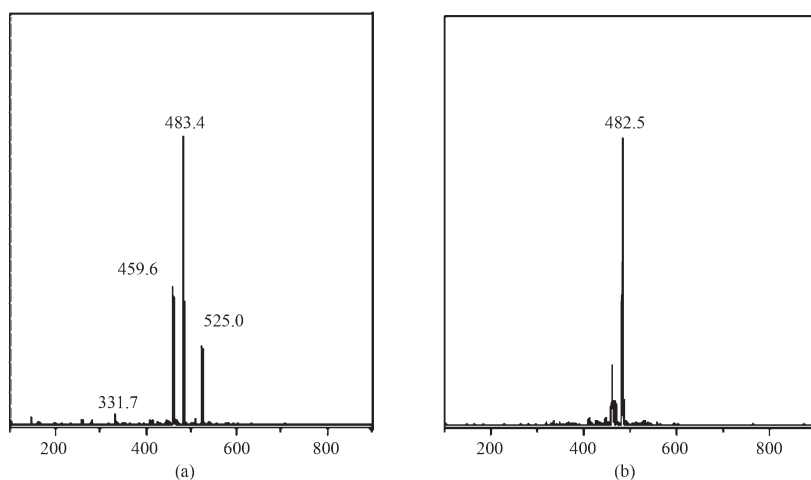


Fig.3 Positive ion ESI-MS of **1** (a) and **2** (b) in methanol solution

### 3 Conclusions

Two new mononuclear copper(II) complexes,  $[\text{CuL}(\text{CH}_3\text{CN})(\text{ClO}_4)]\text{ClO}_4$  (**1**) and *cis*- $[\text{CuL}(\text{NCS})_2] \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (**2**) with 2-[*N,N*-di(2-pyridylmethyl)amino-methyl]-6-aldehyde-4-methylphenol have been synthesized and characterized by UV-Vis, IR, ESI-MS spectra, elemental analysis and X-ray crystal structure analysis. Complex **1** has a distorted octahedral  $[\text{CuN}_4\text{O}_2]$  core, while **2** locates in a distorted octahedral  $[\text{CuN}_5\text{O}]$  core with two  $\text{NCS}^-$  anions in a *cis*-arrangement. The L ligand acts as a tetradentate chelating agent in the complexes.

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