ORIGINAL RESEARCH

# Syntheses and crystal structures of two novel Cu(II) and Co(II) complexes with 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole

Wei Lu · Dun-Ru Zhu · Yan Xu · Hui-Min Cheng · Jian Zhao · Xuan Shen

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Abstract A new ligand, 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L) and its complexes, *trans*-[CuL<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] (1) and *cis*-[CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O· CH<sub>3</sub>OH (2), have been synthesized and characterized by UV, IR, electrospray ionization mass spectrum, elemental analyses, and single-crystal X-ray diffraction methods. In the structure, two L ligands are stabilized by intermolecular  $\pi \cdots \pi$  interactions between the triazole rings. In the complexes, each L ligand adopts a chelating bidentate mode through N atom of pyridyl group and one N atom of the triazole. Both complexes have a similar distorted octahedral [MN<sub>4</sub>O<sub>2</sub>] core (M = Cu<sup>2+</sup> and Co<sup>2+</sup>) with two ClO<sub>4</sub><sup>-</sup> ions in the *trans* position in 1 but two H<sub>2</sub>O molecules in the *cis* arrangement in **2**.

**Keywords** Syntheses · Triazole · Crystal structures · Copper(II) complex · Cobalt(II) complex

## Introduction

Over the past few decades, 1,2,4-triazole derivatives have attracted much attention, mainly because of the fact that these molecules can act as flexible bridging ligands and spacers between transition metal ions [1-3]. Some complexes containing substituted 1,2,4-triazole ligands show

interesting magnetic properties [4–7], especially, some iron(II)–triazole complexes have spin-crossover properties which can be used in molecular electronics [8], as information storage [9] and switching materials [10]. Recently, some 4-substituted 3,5-di(2-pyridyl)-1,2,4-triazoles and their metal complexes have been prepared by us and other groups [11–18]. However, complexes with asymmetrically 3,5-di-substituted 1,2,4-triazole have been little studied so far [19–26]. Herein, we report the syntheses of a new 1,2,4triazole ligand, 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L) and its complexes, *trans*-[CuL<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] (1) and *cis*-[CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·CH<sub>3</sub>OH (2). Their single crystal structures and spectral properties have systematically been investigated.

## **Experimental**

## General

All chemicals used were of analytical grade. Solvents were purified by conventional methods. Melting point was determined using an X4 digital microscopic melting point apparatus, and was uncorrected. Elemental analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectra were recorded on a Nicolet Avatar 380 FT-IR instrument with KBr pellets in the range 4000–400 cm<sup>-1</sup>. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 35 spectrometer at room temperature in acetonitrile solution. The <sup>1</sup>H-NMR spectra were measured with a Bruker AM 500 spectrometer at ambient temperature in CDCl<sub>3</sub> using TMS as internal reference. Electrospray ionization mass spectrum (ESI-MS) was recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH on the mobile phase; the flowrate of the mobile

W. Lu  $\cdot$  D.-R. Zhu  $(\boxtimes) \cdot$  Y. Xu  $\cdot$  H.-M. Cheng  $\cdot$  J. Zhao  $\cdot$  X. Shen

College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China e-mail: zhudr@njut.edu.cn

phase was  $0.2 \text{ cm}^3 \text{ min}^{-1}$ . The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40 V, and 260 °C, respectively.

## Synthesis of L

The ligand, 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (**L**) was synthesized by the reaction of 4,4'dibromophenylphosphazoanilide (2.251 g, 6.05 mmol) and *N*-acetyl-*N*'-(2-pyridoyl)hydrazine (0.985 g, 5.50 mmol) in *o*-dichlorobenzene at 180–190 °C for 3 h [27], yield 0.946 g (54.6%), m.p. 183–185 °C. Colorless single crystals suitable for X-ray analysis were obtained from acetone upon slow evaporation at room temperature. Elemental analyses: found (%): C, 53.47; H, 3.66; N, 17.69. C<sub>14</sub>H<sub>11</sub>BrN<sub>4</sub> Calcd. (%): C, 53.35; H, 3.52; N, 17.78. UV (nm):  $\lambda = 226$ , 281.7. IR (cm<sup>-1</sup>):  $\nu = 3049.5$  m, 3003.6 m, 2921.3 w, 1589.7 m, 1526.2 m, 1491.2 s, 1070 m, 998.4 m. <sup>1</sup>H-NMR  $\delta$ : 2.37 (3H, s), 7.11–7.13 (2H, d), 7.22–7.24 (1H, t), 7.62–7.24 (2H, d), 7.76–7.80 (1H, t), 8.17–8.18 (1H, d), 8.30–8.31 (1H, d).

# Synthesis of *trans*- $[CuL_2(ClO_4)_2]$ (1)

To a solution of L (0.189 g, 0.60 mmol), in boiling EtOH (10 cm<sup>3</sup>), a solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.073 g, 0.30 mmol) in EtOH (5 cm<sup>3</sup>) was added. The mixture was filtered into an EtOH solution containing NaClO<sub>4</sub>·H<sub>2</sub>O (0.084 g, 0.60 mmol). The blue crystalline solid that formed was isolated, washed with H<sub>2</sub>O, and dried in vacuo to yield 0.209 g (85.9%) of the complex. Blue single crystals suitable for X-ray analysis were obtained from a methanol solution. Elemental analyses: found (%): C, 37.49; H, 2.56; N, 12.39. C<sub>28</sub>H<sub>22</sub>Br<sub>2</sub>Cl<sub>2</sub>CuN<sub>8</sub>O<sub>8</sub> Calcd. (%): C, 37.67; H, 2.48; N, 12.55. UV (nm):  $\lambda = 227$ , 289.8. IR (cm<sup>-1</sup>):  $\nu = 3084.4$  w, 2913.1 w, 1614.3 m, 1549.1 m, 1501.1 s, 1112.4–1091.8 s, 1024.6 m, 929.1 m, 624.1 s. ESI-MS: m/z = 792.05, 504.85, 348.53.

Synthesis of cis-[CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·CH<sub>3</sub>OH (2)

Complex **2** was prepared in 81.2% yield by a procedure similar to complex **1** but using CoCl<sub>2</sub>·6H<sub>2</sub>O instead of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O. The pale orange single crystals suitable for X-ray diffraction were obtained by evaporation from a methanol solution. Elemental analyses: found (%): C, 35.57; H, 3.43; N, 11.61. C<sub>29</sub>H<sub>32</sub>Br<sub>2</sub>Cl<sub>2</sub>CoN<sub>8</sub>O<sub>12</sub> Calcd. (%): C, 35.75; H, 3.31; N, 11.50. UV (nm):  $\lambda = 226$ , 282. IR (cm<sup>-1</sup>):  $\nu = 3405.8$  s, 3080.8 w, 2917.4 w, 1607.7 m, 1539.9 m, 1495.4 s, 1144.6–1089.6 s, 1021.4 m, 927.3 m, 636.8 s. ESI-MS: m/z = 787.93, 503.26, 365.42, 344.93.

X-ray data collection and structure determination

The well-shaped single crystals of L, 1, and 2 were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 293(2) K on a Bruker SMART CCD diffractometer with a detector distance of 5 cm and frame exposure time of 10 s using a graphitemonochromated MoK<sub> $\alpha$ </sub> ( $\lambda = 0.71073$  Å) radiation. The structures were all solved by direct methods and refined on  $F^2$  by full-matrix least squares procedures using SHELXTL software [28]. All non-hydrogen atoms were anisotropically refined. Atoms N1, N5, C1, C16, and C17 of the pyridyl rings in the L ligand were found to be disordered over two positions (N1, N1A; N5, N5A; C1, C1A; C16, C16A: and C17. C17A) and fixed at 0.5. Atoms O7. O8. O9, and O10 of one  $ClO_4^-$  anion in 2 were also highly disordered, with an occupancy of 0.540(5) for O7, O8, O9, and O10 and 0.460(5) for O7A, O8A, O9A, and O10A, respectively. All H atoms of organic ligand were generated geometrically and allowed to ride on their respective parent atoms, but not refined. Crystallographic data are summarized in Table 1. The selected bond lengths and angles for L, 1, and 2 are listed in Table 2.

#### **Results and discussion**

#### Syntheses

The asymmetrically 3,5-di-substituted 1,2,4-triazole (**L**) reacts with  $M^{2+}$  (M = Cu and Co) ion and NaClO<sub>4</sub> in molar ratio 2:1:2 to form two neutral monomeric hexacoordinate complexes, *trans*-[CuL<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] (**1**) and *cis*-[CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·CH<sub>3</sub>OH (**2**), which are stable in air. Yields for complexes **1** and **2** are 85.9 and 81.2%, respectively. The elemental analyses were satisfactory and indicate that each complex contains one metal ion, two triazole ligands, and two ClO<sub>4</sub><sup>-</sup> anions except **2** with three water molecules and one methanol molecule.

## Crystal structure of L

The molecular structure of **L** with the atom-numbering scheme is shown in Fig. 1. In the structure, the central 1,2,4-triazole ring is surrounded by a pyridyl group, a methyl group, and a *p*-bromophenyl ring. Meanwhile, the triazole ring of each ligand is superimposed by a forming  $\pi \cdots \pi$  stack with that of one adjacent ligand. The separation of the parallel triazole ring from adjacent one is 3.593 Å, whereas the stacking distance between the two triazole ring centroids is 3.628 Å. It is noticeable that some atoms of the pyridyl group are highly disordered, the occupancy factors for N1, N5, C1, C16, and C17 are all fixed as 0.50. Bond

Compounds	L	1	2
Empirical formula	C <sub>14</sub> H <sub>11</sub> BrN <sub>4</sub>	C <sub>28</sub> H <sub>22</sub> Br <sub>2</sub> Cl <sub>2</sub> CuN <sub>8</sub> O <sub>8</sub>	C <sub>29</sub> H <sub>32</sub> Br <sub>2</sub> Cl <sub>2</sub> CoN <sub>8</sub> O <sub>12</sub>
Formula weight	315.18	892.80	974.28
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/m$	$P2_1/n$	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	11.258(2)	7.8413(16)	9.3232(19)
<i>b</i> (Å)	7.1854(14)	14.723(3)	17.115(3)
<i>c</i> (Å)	17.322(4)	14.396(3)	25.365(5)
α (°)	90	90	90
β (°)	108.59(3)	99.94(3)	90
γ (°)	90	90	90
$V(\text{\AA}^3)$	1328.1(5)	1637.0(6)	4047.4(14)
Ζ	4	2	4
D <sub>c</sub>	1.576	1.811	1.599
$\mu (\mathrm{mm}^{-1})$	3.086	3.334	2.596
F (000)	632	886	1956
Crystal size (mm)	$0.12 \times 0.14 \times 0.32$	$0.10\times0.12\times0.20$	$0.12 \times 0.13 \times 0.24$
$\theta$ range	3.09-25.00	2.98-25.00	3.21-25.00
Reflections collected	11150	13668	31125
Independent reflections	2545 $[R_{int} = 0.067]$	2877 [ $R_{int} = 0.166$ ]	7106 [ $R_{int} = 0.186$ ]
Reflections observed $[I > 2\sigma(I)]$	1861	1502	3343
Data/restraints/parameters	2545/18/232	2877/0/223	7106/160/537
Goodness-of-fit on $F^2$	1.269	1.016	0.989
$R/wR [I > 2\sigma(I)]$	0.0872/0.2412	0.0694/0.1099	0.0843/0.1461
<i>R</i> / <i>w</i> R (all data)	0.1169/0.2514	0.1633/0.1332	0.2007/0.1779
Max., min. $\Delta \rho$ (eÅ <sup>-3</sup> )	0.81, -0.97	0.47, -0.53	0.43, -0.49

Table 2	Selected	bond		
distances	(Å) and	angles	(°)	for
L, 1, and	2			

L		1		2	
N1-C1	1.402(17)	Cu1–N1	2.066(5)	Co1–N1	2.163(5)
N1-C5	1.455(16)	Cu1–N2	1.971(5)	Co1–N2	2.120(5)
N2-N3	1.383(17)	N2-N3	1.371(7)	Co1-N5	2.145(5)
N6-N7	1.383(19)			Co1–N6	2.132(5)
N5-C17	1.380(18)	Cu1–O4	2.565(6)	Co1–O1 W	2.034(4)
N5-C19	1.462(16)			Co1–O2 W	2.076(4)
Br1-C12	1.903(11)	Br1–C12	1.912(7)	Br1–C12	1.862(7)
N4-C6-N2	110.6(12)	O4–Cu1–N1	90.0(2)	O1 W-Co1-O2 W	95.04(19)
N4-C7-N3	110.9(11)	O4-Cu1-N2	81.4(2)	O1 W-Co1-N1	89.17(19)
N4-C7-C8	123.0(11)	N1-Cu1-N2	79.8(2)	N1-Co1-N2	75.25(19)
C7-N4-C6	104.4(11)	N1-Cu1-N2A	100.2(2)	N5-Co1-N6	76.36(19)
C7-N3-N2	106.3(10)	O4–Cu1–O4A	180.0	O1 W-Co1-N5	167.83(19)
N1-C5-C6	118.9(11)	N1–Cu1–N1A	180.0	O2 W-Co1-N1	166.65(19)
		N2-Cu1-N2A	180.0	N2-Co1-N6	176.98(19)

lengths and angles in **L** are comparable with those reported for the related structures [16, 27]. The dihedral angle between the triazole ring and the *p*-bromophenyl ring is  $90.0(1)^{\circ}$ .

# Crystal structure of 1

A projection of the structure of 1 is presented in Fig. 2a together with the atomic labeling system. The complex



Fig. 1 Projection of the structure of L with the atomic labeling system. Hydrogen atoms are omitted for clarity

crystallizes in the monoclinic space group  $P2_1/n$  and there is an inversion center at the copper(II) atom. The copper atom is surrounded by four nitrogen atoms from two L ligands in the equatorial plane and two oxygen atoms from two ClO<sub>4</sub><sup>-</sup> ions in the axial positions to form a distorted octahedral geometry. Each L ligand coordinates to copper atom through N1 atom of the pyridyl ring and N2 atom of the triazole, which is similar to the coordination modes in the related complexes [19–26]. The Cu–N bond lengths are within the normal ranges observed for octahedral complex [19]. However, the Cu–N bond to the triazole nitrogen is 0.095 Å shorter than that to the pyridyl nitrogen. The same feature has been observed in the similar complexes [19–23]. The Cu–O distance is 2.565(6) Å, indicating the involvement of two  $ClO_4^-$  ions in the coordination [29], which is different from that found in a homologous copper(II) complex,  $[CuL'_2](ClO_4)_2$  [21] [L' = 3-ethyl-4-(p-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole] where the  $ClO_4^-$  ions are uncoordinated. The ligand L in 1 is nonplanar. The triazole ring makes dihedral angles of 11.5(2)° and  $66.3(2)^{\circ}$  with the pyridyl ring and *p*-bromophenyl ring, respectively. The crystal structure is further stabilized by weak intermolecular C-H···N [C1-H1A···N3 =  $143^{\circ}$  and  $C1\cdots N3 = 3.134(9)$  Å] and  $C-H\cdots O$  [C4-H4A···O4 =  $132^{\circ}$  and  $C4\cdots O4 = 3.222(9)$  Å;  $C8-H8A\cdots O3 = 155^{\circ}$ and  $C8 \cdots O3 = 3.425(10)$  Å] hydrogen bonds (Fig. 3 and Table 3).

#### Crystal structure of 2

Figure 2b presents the structure of 2 with its atom numbering system. The crystal structure consists of a  $[CoL_2(H_2O)_2]^{2+}$ cation, two  $ClO_4^-$  anions, one lattice water molecule, and one methanol molecule. Similar to 1, the cobalt atom in 2 is also coordinated by four nitrogen atoms from two L ligands and two oxygen atoms from two H<sub>2</sub>O molecules to form a distorted octahedral geometry. However, two coordinated water molecules in 2 are in a cis arrangement, which has not been observed in the complexes with asymmetrically 3,5di-substituted 1,2,4-triazole [19–23]. This feature is also different from that found in a mononuclear cobalt(II) complex with symmetrically 3,5-di-substituted 1,2,4-triazole, **[30]**  $[Co(MBPT)_{2}(H_{2}O)_{2}](ClO_{4})_{2}\cdot 4H_{2}O$ [MBPT = 4-(*p*-methylphenyl)-3,5-*bis*(2-pyridyl)-1,2,4-triazole] where two coordinated water molecules are in a trans oriented. The Co-O(2W) distance is 0.042 Å longer than Co-O(1W) one. whereas the Co-N bond lengths are in the ranges from 2.120(5) to 2.163(5) Å. Although the Co-N<sub>py</sub> bond lengths [2.163(5) and 2.145(5) Å] are longer than the Co–N<sub>trz</sub> bond lengths [2.120(5) and 2.132(5) Å], the difference is smaller than those observed in  $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ . The coordination mode of L ligand in 2 is similar to that found in 1, however, the geometric parameters are quite different. The bond lengths [N1–C5, 1.319(8) Å; N2–N3, 1.403(7) Å; N2–C6, 1.297(7) Å] of L in 2 are different from those [N1-C5, 1.368(8) Å; N2-N3, 1.371(7) Å; N2-C6, 1.310(8) Å] found in 1. These differences are caused mainly by the cations ( $Cu^{2+}$  and  $Co^{2+}$  ions), maybe it can be considered as a "cation effect." The triazole ring with N2 atom makes dihedral angles of  $6.1(2)^{\circ}$  and  $75.2(2)^{\circ}$  with the N1-containing pyridyl ring and Br1-containing phenyl ring, respectively, whereas the triazole ring with N6 atom makes dihedral angles of 5.7(2)° and 66.3(2)° with the N5-containing pyridyl ring and Br2-containing phenyl ring, respectively. One  $ClO_4^-$  anion is highly disordered (54:46) and is connected to the coordinated water by O-H-··O hydrogen bonding. In addition, there are six kinds of intermolecular hydrogen bond interactions in 2: (1) between coordinated water molecules and lattice water [O1W-H1WB···O3W and O2W-H2WB···O3W]; (2) between coordinated water molecules and methanol [O1W-H1WA…O11]; (3) between lattice water and uncoordinated nitrogen atom of the triazole [O3W-H3WA···N3 and O3W-H3WB…N7]; (4) between lattice water and  $ClO_4^{-}$  anion [O3W-H3WA...O9]; (5) between methanol and  $ClO_4^$ anion [O11-H11B···O8]; (6) between hydrogen atoms of the pyridyl ring and ClO<sub>4</sub><sup>-</sup> anion [C3-H3A···O8; C16-H16A…O4; C17–H17A…O4 and C17–H17A····O5] (Table 4). These extensive hydrogen bonds assemble the cation unit, anions, lattice water molecule, and methanol molecule into a three-dimensional structure (Fig. 4).





**Fig. 3** The crystal packing of **1** viewed along the *a*-axis showing the hydrogen bonding

Spectral characterization

The IR spectrum of free L shows two medium bands at 1589.7 and 1526.2 cm<sup>-1</sup>, attributable to the pyridyl ring vibrations. Upon pyridine coordination to a metal the

higher band is shifted by about 15 wavenumbers [31]. So, in the spectrum of the complex 1 (or 2), a band at 1614.3 (or 1607.7) (m) and 1549.1 (or 1539.9) cm<sup>-1</sup> (m) can be assigned to the coordinated pyridyl ring, respectively. This means that in 1 and 2, each L ligand uses one pyridyl

Table 3 The hydrogen bonding geometry of 1

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D–H…A (°)	
C1–H1A…N3 <sup>a</sup>	0.93	2.34	3.134(9)	143	
$C4-H4A\cdots O4^{b}$	0.93	2.53	3.222(9)	132	
C8–H8A…O3 <sup>c</sup>	0.96	2.53	3.425(10)	155	
Symmetry codes: (a) $-x$ , $-y$ , $-z$ ; (b) $-1 + x$ , $y$ , $z$ ; (c) $\frac{1}{2} - x$					

Table 4 The hydrogen bonding geometry of 2

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	D-HA (°)
O1W–H1WB…O3W <sup>a</sup>	0.82	2.00	2.720(7)	145
O1W-H1WA…O11	0.82	1.95	2.649(9)	142
O2W-H2WBO3 W	0.82	2.10	2.705(7)	131
O2W-H2WA…O10 <sup>a</sup>	0.81	2.35	2.987(12)	136
O3W-H3WB…N7 <sup>b</sup>	0.82	2.21	2.871(7)	137
O3W-H3WA…N3	0.83	2.12	2.837(7)	146
O3W-H3WA····O9	0.83	2.60	3.168(11)	127
O11-H11B…O8	0.85	2.56	3.353(14)	156
C3–H3A…O8 <sup>c</sup>	0.93	2.45	3.228(15)	141
C16–H16A…O4 <sup>d</sup>	0.93	2.43	3.178(10)	138
C17-H17A…O4	0.93	2.58	3.268(10)	131
C17–H17A…O5	0.93	2.59	3.464(11)	157
Summatry and as (a)	1/2 + 3	5/2	$\pi(h) = 1$	12 1 11 5/2

Symmetry codes: (a) 1/2 + x, -5/2 - y, -z; (b) -1/2 + x, -5/2 - y, -z; (c) -1 - x, 1/2 + y,  $\frac{1}{2} - z$ ; (d) -1/2 + x, -3/2 - y, -z

nitrogen and one triazole nitrogen for chelate binding. In the complex 1 (or 2), the bands due to the ionic perchlorate groups are around 1112.4–1091.8 (or 1144.6–1089.6) (s), 929.1 (or 927.3) (w), 624.1 (or 636.8) cm<sup>-1</sup> (s), which can

**Fig. 4** The crystal packing of **2** viewed along the *a*-axis showing the hydrogen bonding

be assigned as the IR-allowed v mode, IR-forbidden vmode and the non-degenerate ClO<sub>3</sub> symmetrical bending frequency, respectively [32]. The medium and broad band centered at 3405.8 cm<sup>-1</sup> for **2** is mainly attributed to H–O– H stretching vibrations of the water molecules, suggesting the existence of hydrogen bonding interactions [33]. While the absence of similar high-frequency absorption for **1** suggests that there is no water molecule within the structure. These features are in agreement with the results of X-ray analyses. In addition, the stretching vibrations of C(Ph)–Br bond at 1070, 1024.6, and 1021.4 cm<sup>-1</sup> are attributed to **L**, **1**, and **2**, respectively.

In the UV–Vis spectrum of the complex 1 (or 2) in acetonitrile solution, two intense bands at 227 (or 226) and 289.8 (or 282) nm are attributed to the L  $\pi$ – $\pi$ \* and n– $\pi$ \* transitions in contrast to those (226 and 281.7 nm) in the free L–acetonitrile solution.

The structures of complexes **1** and **2** in solution were also studied by ESI-MS [34–36]. Figure 5a displays the positive ESI-MS of **1** in methanol solution. Three main peaks were observed. The base peak at m/z 792.05 is  $[CuL_2(ClO_4)]^+$  ion and that at m/z 504.85 is  $[CuL_3]^{2+}$ . The peak at m/z 348.53 is  $[CuL_2]^{2+}$ . Figure 5b displays the positive ESI-MS of **2** in methanol solution. Four main peaks were also observed. The peak at m/z 787.93 is  $[CoL_2(ClO_4)]^+$ . The base peak at m/z 503.26 is [CoL $(MeOH)(ClO_4)]^+$ , which is one  $[CoL(ClO_4)]^+$  structure unit containing a solvent molecule in it. The peaks at m/z 344.93 and 365.40 are  $[CoL_2]^{2+}$  and  $[L(H_2O)(MeOH)]^+$ , respectively. Compared to that of  $[Co(bpy)_3(ClO_4)_3]$  [35], the spectrum of the complex **2** in solution showed no sign of the presence of Co(III) complex. It clearly indicates that





Fig. 5 Positive ion ESI-MS of 1 (a) and 2 (b) in methanol solution

there is no chemical reduction/oxidation reaction in the solution and that the complex 2 is also stable in methanol solution. In addition, it should be mentioned that the formation of the different aggregates in the ESI-MS spectra of 1 and 2 can be influenced by the concentration of the complexes [37].

## Conclusion

Two new copper(II) and cobalt(II) complexes with 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (**L**) and its complexes *trans*-[CuL<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] (**1**) and *cis*-[CoL<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O·CH<sub>3</sub>OH (**2**) have been synthesized, and their molecular structures determined by X-ray analyses, IR, and ESI-MS. Structural analyses indicate that both **1** and **2** have a similar pseudo-octahedral [MN<sub>4</sub>O<sub>2</sub>] core with two ClO<sub>4</sub><sup>-</sup> ions in the *trans* position in **1** but two H<sub>2</sub>O molecules in the *cis* arrangement in **2**.

#### Supplementary material

CCDC 751207, 751208, 751209 for compounds L, 1, and 2 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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