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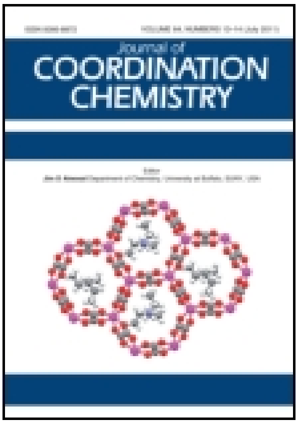

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# Syntheses, crystal structures, and spectral characterization of two new Cu(II) and Co(II) complexes with an asymmetrical substituted triaryltriazole

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# Syntheses, crystal structures, and spectral characterization of two new Cu(II) and Co(II) complexes with an asymmetrical substituted triaryltriazole

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Two new complexes, *trans*-[$CuL_2(ClO_4)_2$] (**1**) and *cis*-[$CoL_2(H_2O)_2$]$(ClO_4)_2 \cdot 2H_2O$ (**2**) with 3-(*p*-methoxyphenyl)-4-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (L), have been synthesized and characterized by elemental analysis, FT-IR, ESI-MS, TGA/DSC, powder XRD, and single crystal X-ray crystallography. Each L in the complexes is chelating bidentate *via* one N of pyridyl and one N of triazole. Both complexes have similar distorted octahedral [$MN_4O_2$] cores ($M = Cu^{2+}$ and $Co^{2+}$) with two $ClO_4^-$ in *trans*-positions in **1** but two $H_2O$ molecules *cis* in **2**.

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

## 1. Introduction

Over the past few decades, substituted 1,2,4-triazole-based ligands have attracted considerable attention in coordination chemistry due to their rich and versatile coordination modes [1–3]. Iron(II) complexes of substituted 1,2,4-triazoles show intriguing spin-crossover properties which can be applied in molecular electronics, such as information storage and switching materials [4–9]. Recently, some $N^4$-substituted-3,5-di(2-pyridyl)-4H-1,2,4-triazole ligands and their metal complexes have been prepared by us [10–17] and other groups [1, 2]. Most recently our attention has focused on preparing asymmetrical 3,4,5-trisubstituted-4H-1,2,4-triazoles and their complexes [18–20]. An asymmetrical triaryltriazole, 3-(*p*-methoxyphenyl)-4-(*p*-chlorophenyl)-5(2-pyridyl)-1,2,4-triazole (L), has been synthesized and structurally characterized [21]. We report herein syntheses of its two new complexes of this ligand, *trans*-[$CuL_2(ClO_4)_2$] (**1**) and *cis*-[$CoL_2(H_2O)_2$]$(ClO_4)_2 \cdot 2H_2O$ (**2**). Their single crystal structures and spectroscopic properties are discussed.

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## 2. Experimental

### 2.1. *Materials and measurements*

All chemicals used were analytical grade. Solvents were purified by conventional methods. Elemental analyses (C, H, N) were recorded with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectra were recorded on a Nicolet Avatar 380 FT-IR instrument with KBr pellets from 4000 to 400 $cm^{-1}$. Electrospray ionization mass spectrum (ESI-MS) was recorded with a LCQ ADVANTAGE MAX mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 $cm^3 min^{-1}$. The spray voltage was 4 KV and the capillary voltage was 40 V. The capillary temperature was 260°C. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a simultaneous NETZSCH STA 449C thermal analyzer under flowing nitrogen from 35 to 800°C at a heating rate of 5°C $min^{-1}$. Powder XRD diffractograms were obtained with a Bruker D8X diffractometer equipped with monochromated Cu-K$\alpha$ ($\lambda = 1.5418$ Å) radiation at room temperature.

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

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.20 mmol) and absolute ethanol (5 $cm^3$) was added dropwise to an ethanol solution (10 $cm^3$) of L (0.145 g, 0.40 mmol) with stirring. The mixture was refluxed for 1 h and then filtered into an ethanol solution containing $NaClO_4 \cdot H_2O$ (0.056 g, 0.40 mmol). The blue crystalline solid that formed was isolated, washed with $H_2O$ and dried in vacuo to obtain the complex (0.175 g, yield 88.8%). Blue single crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution. Anal. Calcd for $C_{40}H_{30}Cl_4CuN_8O_{10}$ (%): C, 48.62; H, 3.06; N, 11.34. Found: C, 48.47; H, 3.21; N, 11.52. FT-IR: 3095 (w), 2942 (w), 1609 (m), 1580 (w), 1500 (s), 1476 (s), 1260 (s), 1108 (s), 1084 (m), 1022 (m), 930 (w), 843 (w), 622 (m) $cm^{-1}$. ESI-MS: $m/z = 888.00$ $[CuL_2(ClO_4)]^+$, 824.58 $[Cu(L\text{-}OCH_3)_2(ClO_4)]^+$, 575.83 $[CuL_3]^{2+}$.

### 2.3. *Synthesis of cis-[$CoL_2(H_2O)_2$]($ClO_4$)$_2 \cdot 2H_2O$ (2)*

Complex **2** was obtained in 79.4% yield by a procedure similar to **1**, but using $CoCl_2 \cdot 6H_2O$ instead of $Cu(NO_3)_2 \cdot 3H_2O$. The light yellow single crystals suitable for X-ray diffraction were obtained by evaporation of an ethanol solution. Anal. Calcd for $C_{40}H_{38}Cl_4CoN_8O_{14}$ (%): C, 45.52; H, 3.63; N, 10.62. Found: C, 45.39; H, 3.91; N, 10.88. FT-IR: 3431 (m, br), 3091 (w), 2942 (w), 1608 (m), 1577 (w), 1493 (s), 1473 (s), 1259 (s), 1112 (s), 1089 (m), 1020 (m), 947 (w), 841 (m), 637 (m) $cm^{-1}$. ESI-MS: $m/z = 884.08$ $[CoL_2(ClO_4)]^+$, 842.33 $[Co(L\text{-}OCH_3)_2(ClO_4)(H_2O)]^+$, 574.08 $[CoL_3]^{2+}$.

### 2.4. *Determination of crystal structures*

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 CCD diffractometer with a detector distance of 5 cm and frame exposure time of 8 s using graphite-monochromated Mo-K$\alpha$ ($\lambda = 0.71073$ Å) radiation. The structures were all solved by direct methods and refined on $F^2$ by full-matrix least-squares using

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

| Complexes | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{40}H_{30}Cl_4CuN_8O_{10}$ | $C_{40}H_{38}Cl_4CoN_8O_{14}$ |
| Formula weight | 988.06 | 1055.51 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ | Aba2 |
| Unit cell dimensions (Å, °) | | |
| $a$ | 8.9107(14) | 34.644(4) |
| $b$ | 30.516(5) | 17.086(3) |
| $c$ | 8.1414(13) | 7.8801(10) |
| $\beta$ | 109.054(2) | 90.00 |
| Volume (Å$^3$), $Z$ | 2092.5(6), 2 | 4664.4(11), 4 |
| $D_c$ (g cm$^{-3}$) | 1.568 | 1.503 |
| $\mu$ (mm$^{-1}$) | 0.846 | 0.670 |
| $F$(000) | 1006 | 2164 |
| Crystal size (mm$^3$) | $0.20 \times 0.12 \times 0.09$ | $0.22 \times 0.14 \times 0.10$ |
| $\theta$ range for data collection (°) | 1.33–25.50 | 1.18–25.00 |
| Reflections collected | 11,769 | 16,165 |
| Independent reflections | 3871 [$R$(int) = 0.0732] | 4122 [$R$(int) = 0.0727] |
| Reflections observed [$I > 2\sigma(I)$] | 2082 | 2655 |
| Data/restraints/parameters | 3871/179/325 | 4122/48/351 |
| Goodness-of-fit on $F^2$ | 0.954 | 0.984 |
| Final $R$ indices [$I > 2\sigma(I)$] | 0.0561/0.1341 | 0.0515/0.1167 |
| $R$ indices (all data) | 0.1246/0.1727 | 0.0978/0.1434 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.327 and −0.400 | 0.327 and −0.229 |

SHELXTL software [22]. All non-hydrogen atoms were anisotropically refined. O2, O3, O4, and O5 of one $ClO_4^-$ in **1** were highly disordered, with an occupancy of 0.826(8) for O2, O3, O4, and O5; and 0.174(8) for O2A, O3A, O4A, and O5A, respectively. O2, O3, O4, and O5 of one $ClO_4^-$ in **2** were also disordered over two positions and fixed at 0.50. All hydrogens of ligand were generated geometrically and allowed to ride on their respective parents, but not refined. Crystallographic data are summarized in table 1. The selected bond lengths and angles for **1** and **2** are listed in table 2. CCDC for **1** and **2** are 824419 and 824420, respectively.

## 3. Results and discussion

### 3.1. *Synthesis*

The asymmetrical substituted triaryltriazole (L) reacts with $M^{2+}$ (M = Cu and Co) and $NaClO_4 \cdot H_2O$ in molar ratio 2 : 1 : 2 to form two monomeric hexacoordinate complexes, *trans*-$[CuL_2(ClO_4)_2]$ (**1**) and *cis*-$[CoL_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ (**2**), which are stable in air. Yields of **1** and **2** are 88.8 and 79.4%, respectively. Elemental analyses were satisfactory and indicate that each complex contains one metal, two triazole ligands, and two $ClO_4^-$ anions; complex **2** contains two coordinated waters and two lattice waters.

### 3.2. *Powder XRD patterns of 1 and 2*

The experimental and simulated XRD patterns of **1** and **2** are shown in figures S1 and S2, respectively. The experimental peak positions are in agreement with the corresponding simulated XRD patterns, which indicate the phase purity of **1** and **2**.

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

| **1** | | **2** | |
|---|---|---|---|
| Cu1–N1 | 2.046(4) | Co1–N1 | 2.178(5) |
| Cu1–N2 | 1.963(4) | Co1–N2 | 2.100(4) |
| Cu1–O5 | 2.415(7) | Co1–O1W | 2.057(4) |
| N2–N3 | 1.370(5) | N2–N3 | 1.379(6) |
| C14–O1 | 1.423(6) | C14–O1 | 1.435(7) |
| C18–Cl1 | 1.728(5) | C18–Cl1 | 1.740(6) |
| N1–Cu1–O5 | 90.2(2) | O1W–Co1–N1 | 90.4(2) |
| N2–Cu1–O5 | 88.8(2) | O1AW–Co1–N2 | 92.6(2) |
| N1–Cu1–N2 | 79.7(2) | N1–Co1–N2 | 75.1(2) |
| N1–Cu1–N2A[a] | 100.3(2) | O1W–Co1–O1AW[b] | 91.2(3) |
| | | O1AW–Co1–N1[b] | 171.3(2) |
| | | N1A–Co1–N2A[b] | 95.7(2) |
| | | N2–Co1–N2A[b] | 167.3(3) |
| C11–O1–C14 | 117.9(4) | C11–O1–C14 | 117.9(5) |

Symmetry codes: [a]$2-x, -y, 2-z$; [b]$-x, -1-y, z$.

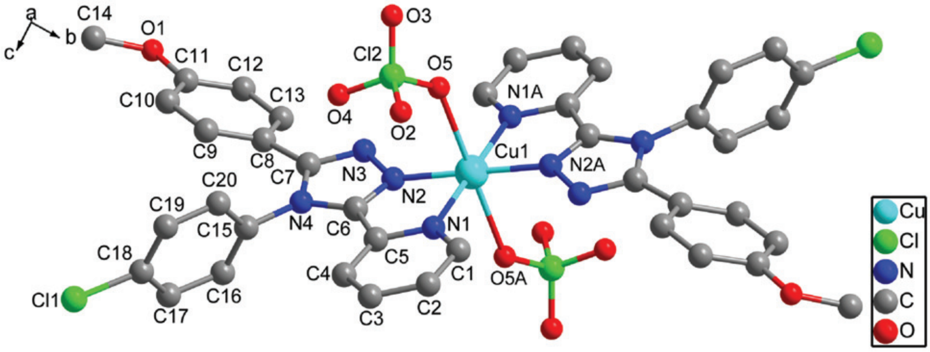

Figure 1. Projection of the structure of **1** with the atomic labeling system. Hydrogens are omitted for clarity.

### 3.3. *Crystal structure of 1*

A projection of the structure of **1** is presented in figure 1, together with the atomic labeling system. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ and there is an inversion center at Cu(II). Each Cu(II) is coordinated with four nitrogens from two L in the equatorial plane and two oxygens from two $ClO_4^-$ ions in axial positions to form a distorted octahedral geometry. Each L coordinates to Cu(II) *via* N1 of the pyridyl ring and N2 of the triazole, similar to coordination modes in analogous Cu(II) complexes [18, 20, 23]. The Cu–O distance is 2.415(7) Å, indicating involvement of two $ClO_4^-$ ions in coordination [24], similar to that found in *trans*-$[CuL^1{}_2(ClO_4)_2]$ [$L^1 = $ 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole] [18] but different from that observed in another Cu(II) complex, $[CuL^2{}_2](ClO_4)_2$ [$L^2 = $ 3-ethyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole] [25], where the $ClO_4^-$ anions are not coordinated. The coordination environment of Cu(II) in **1** is significantly different from that found in a triazole-based Cu(II) complex, $[CuL^3{}_2Cl_2]$ [$L^3 = $ 3,5-di(2-pyridyl)-1,2,4-triazole] [26], where two pyridyl nitrogens and two chlorides coordinate to Cu(II) in an equatorial

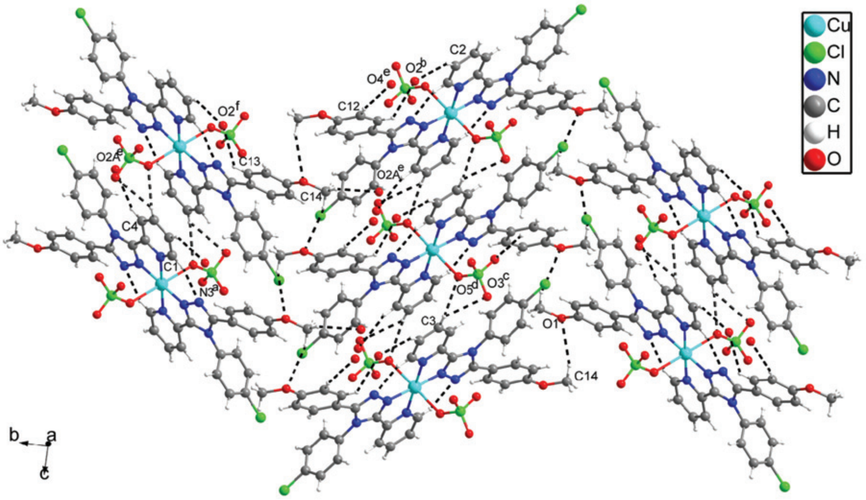

Figure 2. The crystal packing of **1** viewed along the *a* axis showing hydrogen bonding.

Table 3. Hydrogen-bond geometry and $\pi$–$\pi$ stacking interaction for **1**.

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| C1–H1A···N3$^a$ | 0.93 | 2.32 | 3.125(7) | 144 |
| C2–H2A···O2$^b$ | 0.93 | 2.61 | 3.378(6) | 141 |
| C3–H3A···O3$^c$ | 0.93 | 2.76 | 3.459(4) | 133 |
| C3–H3A···O5$^d$ | 0.93 | 2.58 | 3.169(6) | 121 |
| C4–H4A···O2A$^e$ | 0.93 | 2.69 | 3.440(5) | 138 |
| C12–H12A···O4$^e$ | 0.93 | 2.70 | 3.569(4) | 155 |
| C13–H13A···O2$^f$ | 0.93 | 2.78 | 3.480(5) | 133 |
| C14–H14A···O2A$^e$ | 0.96 | 2.64 | 3.468(6) | 145 |
| C14–H14B···O1 | 0.96 | 2.79 | 3.710(6) | 167 |
| C4–H4A···$\pi$ (*p*-Cl-Ph) | 0.93 | 3.08 | 3.889(5) | 147 |
| C9–H9A···$\pi$ (*p*-Cl-Ph) | 0.93 | 2.87 | 3.629(7) | 140 |
| $\pi$···$\pi$ interaction | cent···cent | $\pi$···$\pi$ |  | dihedral angle |
| $\pi$ (py)···$\pi$ (py)$^g$ | 4.123 | 3.748 |  | 0.0 |

Symmetry codes: $^a2-x, -y, 2-z$; $^b3-x, -y, 2-z$; $^c1-x, -y, 2-z$; $^dx, y, z-1$; $^ex-1, y, z-1$; $^fx-1, y, z$; $^g-x, 1-y, 2-z$.

plane while two triazole nitrogens are axial. The L in **1** is not co-planar. The dihedral angles between the central triazole ring and the pryidyl and *p*-methoxyphenyl ring in **1** are 8.3(2)° and 25.4(2)°, which are smaller than those found in free L (23.7(2)° and 30.4(2)°) [21], whereas a dihedral angle between the triazole ring and the *p*-chlorophenyl ring in **1** is 75.9(2)°, which is close to that observed in free L (73.5(2)°).

There are four kinds of intermolecular and intramolecular hydrogen bonds in **1** (figure 2 and table 3), which is significantly associated with the crystal packing. These hydrogen bond interactions are: (1) between pyridyl and triazole [C1–H1A···N3$^a$]; (2) between two methoxy groups [C14–H14B···O1]; (3) between pyridyl and $ClO_4^-$ [C2–H2A···O2$^b$, C3–H3A···O3$^c$, C3–H3A···O5$^d$, C4–H4A···O2A$^e$]; (4) between *p*-methoxyphenyl and $ClO_4^-$ [C12–H12A···O4$^e$, C13–H13A···O2$^f$, C14–H14A···O2A$^e$]. Moreover, there are two kinds of intramolecular edge-to-face C–H···$\pi$

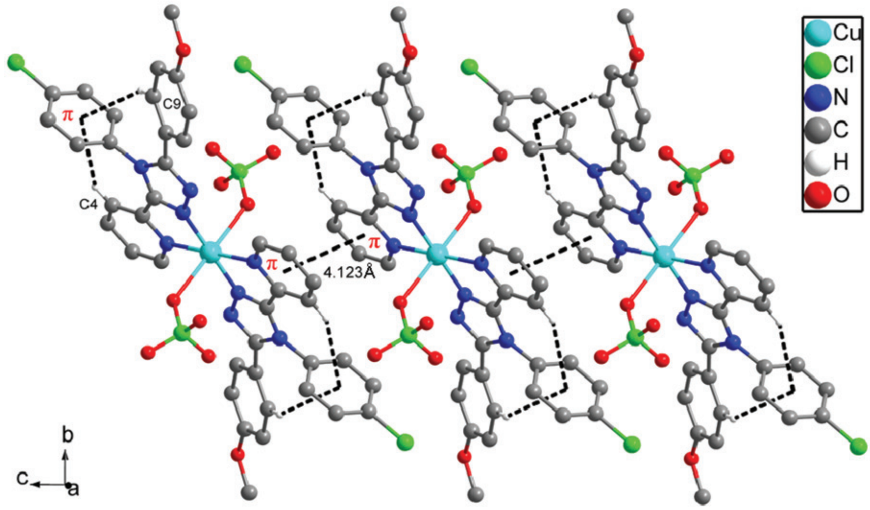

Figure 3. View of C$\cdots$H–$\pi$ and $\pi$–$\pi$ stacking interactions in **1**. Some hydrogen atoms have been omitted for clarity.

interactions in **1** involving C4–H4A and C9–H9A, respectively, and *p*-chlorophenyl ring (H4A$\cdots\pi = 3.08$ Å and C4–H4A$\cdots\pi = 147°$; H9A$\cdots\pi = 2.87$ Å and C9–H9A$\cdots\pi = 140°$) (figure 2 and table 3). An offset face-to-face $\pi$–$\pi$ interaction exists between two parallel pyridyl groups with a plane–plane distance of 3.748 Å and a centroid–centroid distance of 4.123 Å (figure 3 and table 3). These extensive hydrogen bonds and $\pi$–$\pi$ stacking interactions assemble the cation units and $ClO_4^-$ anions into a 3-D structure.

### 3.4. *Crystal structure of 2*

Figure 4 presents the structure of **2** with its atom numbering system. Complex **2** crystallizes in the orthorhombic space group Aba2. The crystal structure consists of a $[CoL_2(H_2O)_2]^{2+}$ cation, two $ClO_4^-$ anions and two lattice waters. Similar to **1**, the Co(II) in **2** is coordinated by four nitrogens from two L and two oxygens from two waters to form a distorted octahedral geometry. However, coordinated waters in **2** occupy *cis* positions, different from an analogous Co(II) complex, $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ [MBPT = 4-(*p*-methylphenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole] [12] where two coordinated water molecules are *trans*. This feature has rarely been observed in complexes with asymmetrical 3,5-di-substituted 1,2,4-triazole [18, 19, 27, 28]. The Co–O distance (2.057(4) Å) is smaller than that found in $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ [12], whereas the Co–N bond lengths in the structure are in the normal range. Although the Co–$N_{py}$ bond lengths (2.178(5) Å) are also longer than the Co–$N_{trz}$ bond lengths (2.100(4) Å), the difference is larger than those observed in $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ [12] and $[CoL^1{}_2(H_2O)_2](ClO_4)_2 \cdot H_2O \cdot CH_3OH$ [18]. The coordination mode of L in **2** is similar to that found in **1**; however, the geometric parameters are quite different. The bond lengths [N1–C1, 1.332(6); C14–O1, 1.423(6); C18–Cl1, 1.728(5) Å] of **L** in **2** are slightly different from those [N1–C1,

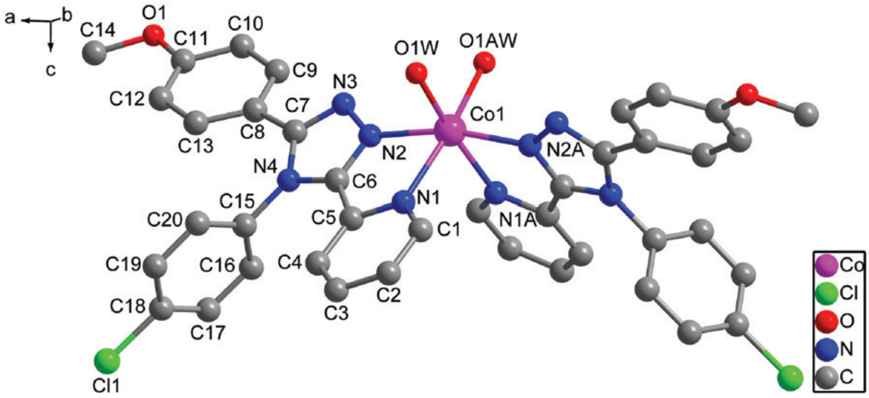

Figure 4. Projection of the structure of **2** with the atomic labeling system. Hydrogen atoms, $ClO_4^-$ and lattice water molecules are omitted for clarity.

Table 4. Hydrogen-bond geometry and C–H···π stacking interaction for **2**.

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| O1W–H1WA···O3[a] | 0.91 | 1.85 | 2.703(4) | 155 |
| O1W–H1WA···O5A[a] | 0.91 | 2.00 | 2.868(5) | 159 |
| O1W–H1WB···O2W[b] | 0.91 | 1.83 | 2.718(7) | 165 |
| O2W–H2WB···O2[c] | 0.84 | 2.69 | 3.501(5) | 163 |
| O2W–H2WB···O3A | 0.84 | 2.07 | 2.790(6) | 144 |
| C2–H2A···O3[d] | 0.93 | 2.60 | 3.428(4) | 148 |
| C2–H2A···O3A[d] | 0.93 | 2.64 | 3.420(5) | 141 |
| C10–H10A···O2 | 0.93 | 2.60 | 3.180(6) | 121 |
| C10–H10A···O2A | 0.93 | 2.63 | 3.410(5) | 142 |
| C14–H14A···O2A[e] | 0.96 | 2.80 | 3.329(6) | 116 |
| C14–H14C···O1[f] | 0.96 | 2.68 | 3.589(4) | 158 |
| C16–H16A···O5[f] | 0.93 | 2.72 | 3.544(5) | 148 |
| C19–H19A···O1[e] | 0.93 | 2.62 | 3.527(7) | 165 |
| C20–H20A···O2A[a] | 0.93 | 2.48 | 3.370(6) | 160 |
| C20–H20A···O4[c] | 0.93 | 2.71 | 3.562(4) | 152 |
| C1–H1A···π (trz) | 0.93 | 3.15 | 3.879(7) | 136 |
| C4–H4A···π (*p*-Cl-Ph) | 0.93 | 2.95 | 3.779(4) | 150 |
| C13–H13A···π (*p*-Cl-Ph) | 0.93 | 2.95 | 3.696(6) | 138 |
| C14–H14B···π (*p*-$CH_3O$-Ph) | 0.96 | 3.40 | 3.914(7) | 116 |

Symmetry codes: [a]$x, y-1/2, 1/2+z$; [b]$-x, -1-y, z$; [c]$x, 1+y, 1+z$; [d]$-x, -1-y, 1+z$; [e]$1/2-x, y, z-1/2$; [f]$x, 1+y, 2+z$.

1.321(7); C14–O1, 1.435(7); C18–Cl1, 1.740(6) Å] found in **1**. Four rings of L in **2** also do not share a common plane. The central triazole ring makes dihedral angles of 10.3(2)° and 20.9(3)° with the pyridyl group and *p*-methoxyphenyl ring, respectively. These dihedral angles are smaller than the corresponding ones found in free L [21]. However, a dihedral angle of 83.9(3)° between the triazole ring and the *p*-chlorophenyl ring in **2** is larger than 73.5(2)° observed in the free L ligand.

Nine kinds of intermolecular and intramolecular hydrogen bonds are observed in the structure of **2** (table 4 and figure 5). These hydrogen bond interactions are: (1) between coordinated waters and $ClO_4^-$ [O1W–H1WA···O3[a], O1W–H1WA···O5A[a]];

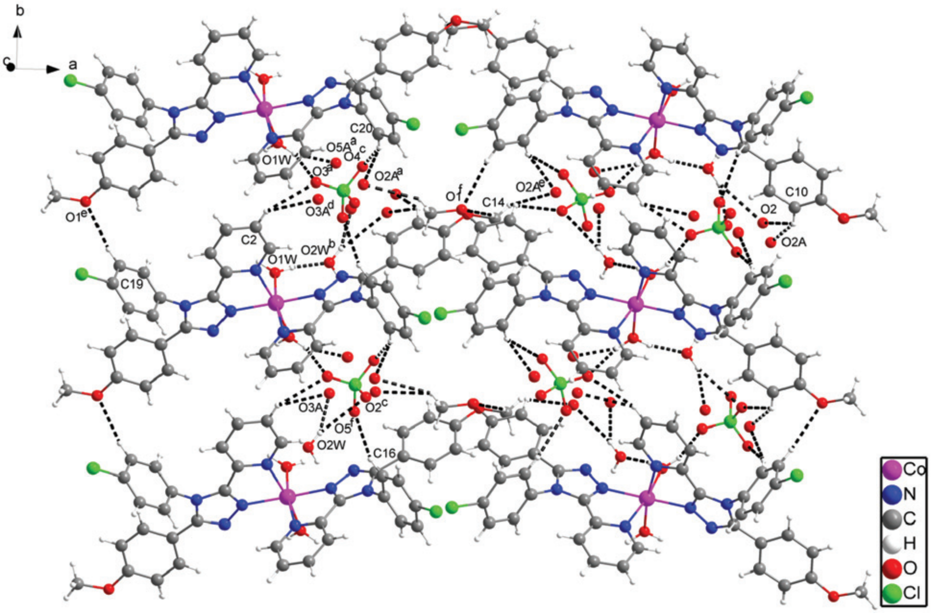

Figure 5. The crystal packing of **2** viewed along the *c* axis showing the hydrogen bonding.

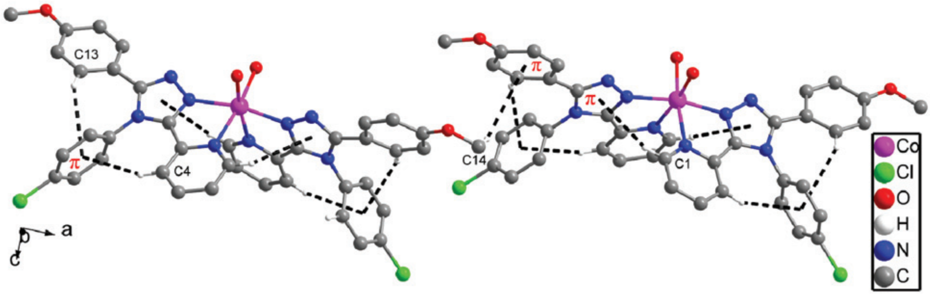

Figure 6. View of four edge-to-face C–H $\cdots\pi$ stacking interactions in **2**. Some hydrogens have been omitted for clarity.

(2) between coordinated water and lattice water [O1W–H1WA $\cdots$ O2W$^b$]; (3) between lattice water and $ClO_4^-$ [O2W–H2WB $\cdots$ O2$^c$, O2W–H2WB $\cdots$ O3A]; (4) between pyridyl and $ClO_4^-$ [C2–H2A $\cdots$ O3$^d$, C2–H2A $\cdots$ O3A$^d$]; (5) between *p*-methoxyphenyl and $ClO_4^-$ [C10–H10A $\cdots$ O2, C10–H10A $\cdots$ O2A]; (6) between methoxy and $ClO_4^-$ [C14–H14A $\cdots$ O2A$^e$]; (7) between two methoxy groups [C14–H14C $\cdots$ O1$^f$]; (8) between *p*-chlorophenyl and methoxy [C19–H19A $\cdots$ O1$^e$]; (9) between *p*-chlorophenyl and $ClO_4^-$ [C16–H16A $\cdots$ O5$^f$, C20–H20A $\cdots$ O2A$^a$, C20–H20A $\cdots$ O4$^c$]. In addition, different from **1**, complex **2** is further stabilized by four kinds of weak C–H $\cdots\pi$ interactions involving (1) C1–H1A and the 1,2,4-triazole, (2) C4–H4A and the *p*-chlorophenyl ring, (3) C13–H13A and the *p*-chlorophenyl ring, and (4) C14–H14B and *p*-methoxyphenyl ring (table 4 and figure 6).

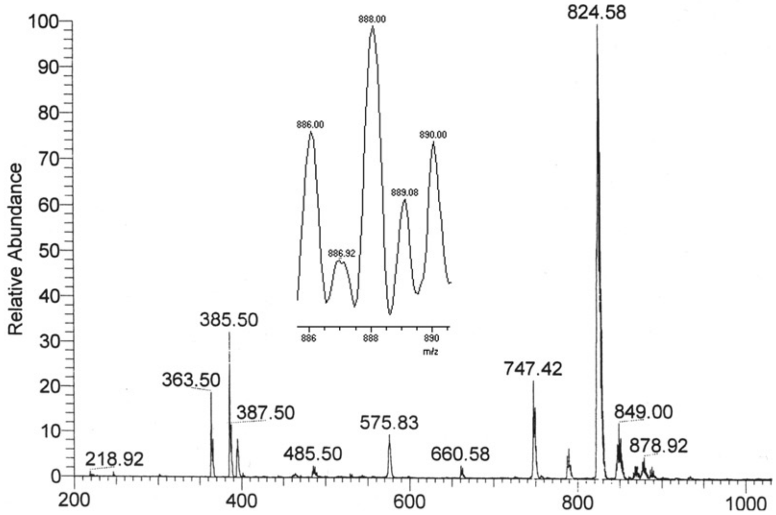

Figure 7. Positive ion ESI-MS spectra of **1** in methanol solution. The inset shows the isotopic patterns of the *m*/*z* 888.00 peak.

### 3.5. *IR spectrum*

The IR spectrum of free L shows two medium bands at 1586 and 1561 cm$^{-1}$, attributable to pyridyl ring vibrations. Upon coordination, the higher band of pyridine can shift about 15 wavenumbers [12]. In the spectrum of **1** (or **2**), a band at 1609 (or 1608) (m) and 1580 (or 1577) cm$^{-1}$ (m) can be assigned to coordinated pyridyl. Thus in **1** and **2**, each L uses one pyridyl nitrogen and one triazole nitrogen for chelate binding. In **1** (or **2**), bands due to ionic perchlorate are 1112 (1100) (s), 930 (947) (w), 622 (637) cm$^{-1}$ (m), which can be assigned as the IR-allowed $\nu$ mode, IR-forbidden $\nu$ mode and nondegenerate $ClO_3$ symmetrical bending frequency, respectively [18]. The medium and broad band centered at 3431 cm$^{-1}$ for **2** is due to H–O–H stretching vibrations of water, suggesting the existence of hydrogen bonding interactions [29]. The absence of a similar high frequency absorption for **1** suggests that there is no water within the structure. These features are in agreement with the results of X-ray analyses. In addition, the stretching vibrations of C(Ph)–Cl at 1084 and 1089 cm$^{-1}$ are attributed to **1** and **2**, respectively.

### 3.6. *Thermal analyses of 1 and 2*

Due to lack of a guest molecule in **1**, TGA (figure S3) shows a high thermal stability. Practically no weight loss was observed up to 290°C. An abrupt weight loss was observed above 290°C because of the decomposition of the ligands, associated with an exothermic peak at 313°C in the DSC curve of **1**. As we can see from the TGA/DSC diagram (figure S4), two main thermal decomposition processes can be observed for **2**. The first weight loss of 6.33% in the range 35–135°C corresponds to removal of two lattice and two coordinated waters (the calculated value is 6.83%), associated with an endothermic peak at 120°C in the DSC curve. The second sharp weight loss occurs

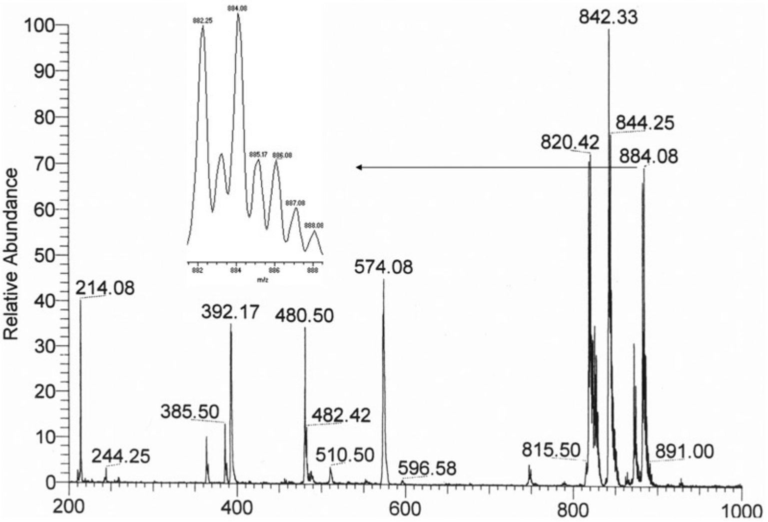

Figure 8. Positive ion ESI-MS spectra of **2** in methanol. The inset shows the isotopic patterns of the *m*/*z* 884.08 peak.

above 345°C due to decomposition of the ligands, associated with an exothermic peak at 345°C in the DSC curve of **2**. The thermal decomposition features of **1** and **2** are in good agreement with their crystal structures.

### 3.7. *Electrospray ionization mass spectrometry (ESI-MS)*

The structures of **1** and **2** in solution were also studied by ESI-MS [30–32]. Figure 7 displays the positive ESI mass spectrum of **1** in methanol and the inset shows the isotopic patterns of the molecular ion peaks. The molecular ion peak at *m*/*z* 888.00 is $[CuL_2(ClO_4)]^+$ (Calcd 888.62) [30]. The base peak at *m*/*z* 824.58 is $[Cu(L\text{-}OCH_3)_2(ClO_4)]^+$ ion. The peak at 575.83 is $[CuL_3]^{2+}$ (Calcd 575.99) and its isotopic patterns are shown in figure S5. Figure 8 displays the positive ESI mass spectrum of **2** in methanol solution and the inset shows the isotopic patterns of the molecular ion peaks. Three main peaks were observed. The molecular ion peak at *m*/*z* 884.08 is $[CoL_2(ClO_4)]^+$ (Calcd 884.01) [30] and the base peak at *m*/*z* 842.33 is $[Co(L\text{-}OCH_3)_2(ClO_4)(H_2O)]^+$. The peak at *m*/*z* 574.08 is $[CoL_3]^{2+}$ (Calcd 573.68) and its isotopic patterns are shown in figure S6.

## 4. Conclusions

Some triazole-based mono- [12, 15, 17–20, 23, 26, 33], di- [34], trinuclear Cu(II) and Co(II) complexes [35–37] and even polymers [38] have been reported. Liu and Ding [33] synthesized a mixed-ligand Cu(II) complex, $[CuL^4(en)_2]_2[Cu(en)_2](ClO_4)_6 \cdot 2L^4$ ($L^4$ = 4-(2-pyridyl)-1,2,4-triazole, en = ethylenediamine) consisting of three independent cations with two five-coordinate [$CuL^4(en)_2$] units and a four-coordinated [$Cu(en)_2$] unit. Using $L^4$ as only bidentate bridging ligand, Ding *et al.* [36] also reported an interesting linear trinuclear cobalt(II) complex, [$Co_3L^4{}_6(H_2O)_6$]($NO_3$)$_6$. Another linear trinuclear Cu(II) complex, [$Cu_3(NTA)_2(4,4'\text{-bpt})_4(H_2O)_2$] · $10H_2O$ ($H_3NTA$ = nitrilotriacetic acid, 4,4′-bpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole), shows an interesting Cu($D_{3h}$)–Cu($O_h$)–Cu($D_{3h}$) coordination mode with each 4,4′-bpt acting as a bismonodentate ligand [35]. Li *et al.* [38] prepared two Co(II) coordination polymers with 1,3,5-tri(1,2,4-triazole-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb), [$Co_3(ttmb)_2(H_2O)_6Cl_6$] · $3H_2O$ and [$Co(ttmb)_2(H_2O)_2$]($NO_3$)$_2$ · $4H_2O$. The former contains a highly undulated 2-D network while the latter has a 2-D (4,4) planar network.

Two new monomeric Cu(II) and Co(II) complexes with 3-(*p*-methoxyphenyl)-4-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (L), *trans*-[$CuL_2(ClO_4)_2$] (**1**) and *cis*-[$CoL_2(H_2O)_2$]($ClO_4$)$_2$ · $2H_2O$ (**2**) have been synthesized. Their molecular structures were determined by X-ray crystallography, IR TGA/DSC, powder XRD and ESI-MS. Both exist as pseudo-octahedral [$MN_4O_2$] cores with two $ClO_4^-$ ions in the *trans*-arrangements in **1** but two $H_2O$ molecules in the *cis*-positions in **2**. Exploration of the iron(II) spin-crossover complexes with the L ligand is currently in progress [39].

## Supplementary material

The simulated and experimental P-XRD patterns, TGA/DSC curves, and the partial isotopic patterns of ESI-MS of **1** and **2**. Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 824419 (**1**) and 824420 (**2**). Copies of the data can be obtained free of charge *via* www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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