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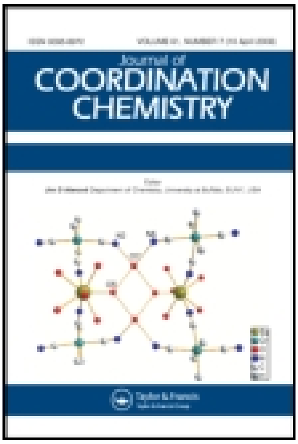

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Syntheses, crystal structures, and spectral properties of Mn(II) and Co(II) complexes with 3-(p-chlorophenyl)- 4-(p-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole

Jian Zhao [a], Hui-Min Cheng [a], Guo-Ping Shen [a], Yan Xu [a] & Dun-Ru Zhu [a]

[a] State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P.R. China

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Syntheses, crystal structures, and spectral properties of Mn(II) and Co(II) complexes with 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole

JIAN ZHAO, HUI-MIN CHENG, GUO-PING SHEN, YAN XU
and DUN-RU ZHU*

State Key Laboratory of Materials-oriented Chemical Engineering,
College of Chemistry and Chemical Engineering, Nanjing
University of Technology, Nanjing 210009, P.R. China

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Two new complexes, *trans*-[$MnL_2(NCS)_2$] (**1**) and *trans*-[$CoL_2(H_2O)(EtOH)$]$(ClO_4)_2 \cdot H_2O$ (**2**) with asymmetrical triaryltriazole ligands [L = 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole], have been synthesized and characterized by elemental analysis, FT-IR, ESI-MS, and single-crystal X-ray diffraction. In the complexes each L adopts a chelating bidentate mode *via* the nitrogen of pyridyl and triazole. Both complexes have a similar distorted octahedral core with two NCS^- ions in the *trans* position in **1**, while one H_2O and one EtOH are present in the axial sites in **2**.

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

1. Introduction

Substituted 1,2,4-triazoles have been studied in coordination chemistry because their complexes have interesting structures and specific magnetic properties [1–4]. Some iron(II) complexes containing substituted 1,2,4-triazole ligands have spin-crossover properties [5, 6], which could be used as molecular-based memory devices, displays, and optical switches [7]. 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 [2, 8–12]. However, complexes with asymmetrically 3,4,5-triaryl-substituted 1,2,4-triazoles have been less studied [13, 14]. As a continuation of our investigation of asymmetrically substituted 1,2,4-triazoles [15, 16], we present here the syntheses of a new triaryltriazole ligand, 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) and its complexes, *trans*-[$MnL_2(NCS)_2$] (**1**) and *trans*-[$CoL_2(H_2O)(EtOH)$]$(ClO_4)_2 \cdot H_2O$ (**2**). Their single crystal structures and spectroscopic properties are also discussed.

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*Corresponding author. Email: zhudr@njut.edu.cn

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2. Experimental

2.1. *Materials and measurements*

All chemicals were of analytical grade. Solvents were purified by conventional methods. Melting point was determined using an X4 digital microscopic melting point apparatus and is uncorrected. Elemental analyses (C, H, N, and S) 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 from 4000 to 400 cm^{-1}. ^{1}H NMR spectra were measured with a Bruker AM 500 spectrometer at ambient temperature in $CDCl_3$ using TMS as the internal reference. Electrospray ionization-mass spectra (ESI-MS) were recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH as 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.

2.2. *Preparation of L*

The ligand, 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L) was synthesized by the reaction of 4,4′-dimethylphenylphosphazoanilide (3.392 g, 14.0 mmol) and *N*-(*p*-chlorophenylcarbonyl)-*N*′-(2-pyridylcarbonyl)hydrazine (3.722 g, 13.5 mmol) in *N*,*N*-dimethylaniline (65 mL) at 190–195°C for 3 h [15]; yield 2.158 g (46.2%), m.p. 187–189°C. Anal. Calcd for $C_{20}H_{15}ClN_4$ (%): C, 69.26; H, 4.36; N, 16.15. Found (%): C, 69.01; H, 4.46; N, 16.03. IR (KBr, cm^{-1}): 3036s, 2922w, 1585m, 1567m, 1513m, 1462s, 1450s, 1417m, 1391w, 1164w, 1092m, 1014m, 974m, 834m, 733m, 605m. ^{1}H NMR δ: 2.43 (3H, s), 7.09–7.11 (2H, d), 7.20–7.21 (2H, d), 7.23–7.25 (1H, t), 7.28–7.30 (2H, d), 7.40–7.42 (2H, d), 7.77–7.79 (1H, t), 8.08–8.09 (1H, d), 8.38–8.39 (1H, d). MS: $m/z = 347.33$.

2.3. *Preparation of trans-[$MnL_2(NCS)_2$] (1)*

To a solution of L (0.139 g, 0.40 mmol), in boiling EtOH (10 cm^3), a solution of $Mn(OAc)_2 \cdot 4H_2O$ (0.049 g, 0.20 mmol) in EtOH (5 cm^3) was added. The mixture was filtered into an EtOH solution containing KSCN (0.039 g, 0.40 mmol). The yellow crystalline solid that formed was isolated, washed with H_2O, and dried *in vacuo* to yield 0.142 g (82.1%) of the complex. Yellow single crystals suitable for X-ray analysis were obtained from an ethanol solution. Anal. Calcd for $C_{42}H_{30}Cl_2MnN_{10}S_2$ (%): C, 58.34; H, 3.50; N, 16.20; S, 7.42. Found (%): C, 58.27; H, 3.59; N, 16.01; S, 7.52. IR (KBr, cm^{-1}): 2064vs, 1599m, 1577m, 1513m, 1476m, 1462s, 1400s, 1090m, 739m, 612m. ESI-MS: $m/z = 805.83$, 807.38.

2.4. *Preparation of trans-[$CoL_2(H_2O)(EtOH)$]$(ClO_4)_2 \cdot H_2O$ (2)*

Complex **2** was prepared in 80.5% yield by a procedure similar to **1** but by using $Co(OAc)_2 \cdot 4H_2O$ and $NaClO_4 \cdot H_2O$ instead of $Mn(OAc)_2 \cdot 4H_2O$ and KSCN, respectively. Light yellow single crystals suitable for X-ray diffraction were obtained by evaporation from an ethanol solution. Anal. Calcd for $C_{42}H_{40}Cl_4CoN_8O_{11}$ (%): C, 48.81; H, 3.90; N, 10.84. Found (%): C, 48.69; H, 3.98; N, 10.76. IR (KBr, cm^{-1}): 3431(m, b),

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

Complexes	**1**	**2**
Empirical formula	$C_{42}H_{30}Cl_2MnN_{10}S_2$	$C_{42}H_{40}Cl_4CoN_8O_{11}$
Formula weight	864.72	1033.55
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁/c*	*P2₁/c*
Unit cell dimensions (Å, °)		
a	13.540(3)	16.297(5)
b	9.394(19)	8.788(3)
c	16.371(3)	16.713(5)
β	101.42(3)	96.886(5)
Volume (Å^3), *Z*	2041.2(7), 2	2376.2(13), 2
Calculated density (g cm^{-3})	1.407	1.445
Absorption coefficient (mm^{-1})	0.601	0.652
F(000)	886	1062
Crystal size (mm^3)	0.08 × 0.18 × 0.4	0.12 × 0.20 × 0.42
θ range for data collection (°)	3.10–25.50	2.46–25.02
Reflections collected	17,564	14,051
Independent reflections	3793 ($R_{\text{int}} = 0.0758$)	4176 ($R_{\text{int}} = 0.0717$)
Reflections observed	2662	2359
Data/restraints/parameters	3793/0/259	4176/49/322
Goodness-of-fit on F^2	1.063	1.034
Final *R* indices ($I > 2\sigma(I)$)	$R_1 = 0.0590$, $wR_2 = 0.0995$	$R_1 = 0.0649$, $wR_2 = 0.1704$
R indices (all data)	$R_1 = 0.0960$, $wR_2 = 0.1093$	$R_1 = 0.1180$, $wR_2 = 0.1942$
Largest difference peak and hole (e Å^{-3})	0.242, −0.274	0.599, −0.403

3077w, 2923w, 1604m, 1576m, 1512s, 1487s, 1468s, 1403m, 1303m, 1093vs, 1030m, 930w, 834s, 711s, 625s. ESI-MS: $m/z = 850.48$, 550.84, 377.24.

2.5. *Crystal structure determination*

Well-shaped single crystals of **1** and **2** were selected for X-ray diffraction. 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 graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL software [17]. All non-hydrogen atoms were anisotropically refined. Atoms C21, C22, and O5 of the ethanol and O1W, O2W, and O2WA of **2** are disordered. The occupation factor of C21, C22, O5, and O1W is 0.5, while the occupation factor of O2W and O2WA is 0.25. O1W and O5 were refined with the same coordinates and anisotropic thermal parameters. Due to disorder, the thermal parameters of partially occupied atoms, C–C and C–O distances in ethanol are restrained during the refinement. All hydrogens of organic ligand were generated geometrically and allowed to ride on their respective parent atoms, but not refined. Details on the crystal data are listed in table 1.

3. Results and discussion

3.1. *Synthesis*

Asymmetrically 3,4,5-triaryl-substituted 1,2,4-triazole (L) reacts with M^{2+} (M = Mn, Co) and KSCN (or $NaClO_4 \cdot H_2O$) in molar ratio 2 : 1 : 2 to form two neutral

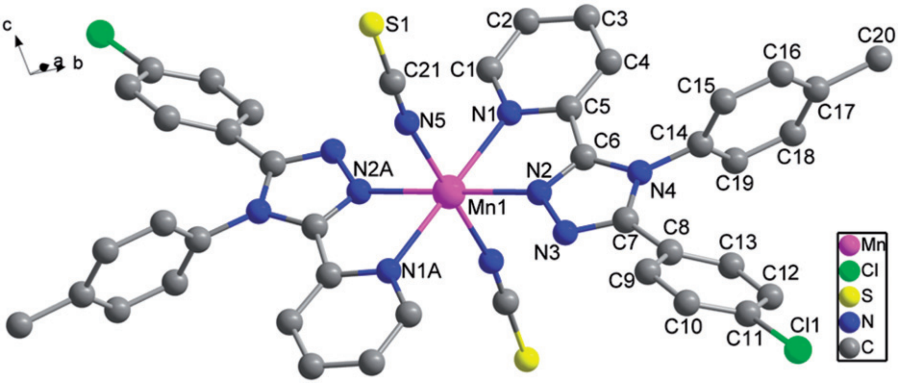

Figure 1. Projection of the structure of **1** with the atomic labeling system. Hydrogens are omitted for clarity.

monomeric hexacoordinate complexes, *trans*-$[MnL_2(NCS)_2]$ (**1**) and *trans*-$[CoL_2(H_2O)(EtOH)](ClO_4)_2 \cdot H_2O$ (**2**), which are stable in air. Yields for **1** and **2** are 82.1% and 80.5%, respectively. Elemental analyses were satisfactory and indicate that **1** contains one Mn(II), two triazole ligands, and two NCS^-, while **2** contains one Co(II), two triazole ligands, two ClO_4^-, two water molecules, and one ethanol.

3.2. *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 Mn(II). Each Mn(II) is surrounded by four nitrogens from two L in the equatorial plane and two NCS^- in the axial positions to form a distorted octahedral geometry. Each L coordinates to Mn(II) *via* N1 of pyridyl and N2 of the triazole, similar to coordination modes in related complexes [15, 16]. The selected bond lengths and angles for **1** are listed in table 2. The Mn–N bond lengths are within the normal ranges observed for octahedral complexes [18, 19]. However, the Mn–N bond to the triazole nitrogen is 0.054 Å shorter than that to the pyridyl nitrogen. The same feature has been observed in analogous complexes with *trans*-NCS^- groups [9, 20, 21]. The NCS^- are almost linear [N5–C21–S1 179.6(4)°], whereas the Mn–NC(S) linkages are a little bent [Mn1–N5–C21 170.8(3)°]. L in **1** is non-planar. The triazole ring makes dihedral angles of 11.2(3)°, 33.9(3)°, and 79.1(3)° with the pyridyl ring, *p*-chlorophenyl ring, and *p*-methylphenyl ring, respectively. Due to a dihedral angle (81.3(3)°) between the pyridyl ring and the *p*-methylphenyl ring in L, there is an intramolecular edge-to-face $C–H \cdots \pi$ interaction involving C4–H4 and the *p*-methylphenyl ring ($H4 \cdots \pi = 2.889$ Å and $\angle C4–H4 \cdots \pi = 151°$). The crystal structure is further stabilized by weak intermolecular $C–H \cdots Cl$ [$C15 \cdots Cl1 = 3.600$ Å and $\angle C15–H15A \cdots Cl1 = 153°$] hydrogen bonds (table 3 and figure 2).

3.3. *Crystal structure of 2*

Figure 3 presents the structure of **2** with its atom numbering system. The crystal structure consists of $[CoL_2(H_2O)(EtOH)]^{2+}$, two ClO_4^-, and one H_2O. In **2**, the Co(II) is

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

1		**2**	
Mn1–N1	2.282(3)	Co1–N1	2.147(4)
Mn1–N2	2.228(3)	Co1–N2	2.073(4)
Mn1–N5	2.182(3)	Co1–O5	2.125(3)
N5–C21	1.152(4)	Co1–O1w	2.125(3)
S1–C21	1.623(4)	–	–
C11–Cl1	1.749(3)	C11–Cl1	1.743(5)
N2–N3	1.382(3)	N2–N3	1.375(5)
N1–Mn1–N2	72.9(1)	N1–Co1–N2	76.8(2)
N1–Mn1–N5	92.4(1)	N1–Co1–O5	90.6(1)
N2–Mn1–N5	87.3(1)	N2–Co1–O5	89.8(2)
N5–C21–S1	179.6(4)	–	–
Mn1–N5–C21	170.8(3)	–	–

Table 3. Hydrogen-bond geometry and π-stacking interaction for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
C15–H15A···Cl[a]	0.930	2.745	3.600(4)	153
C4–H4A···π (C14–19)	0.929	2.889	3.731(4)	151

Symmetry code: [a] x, $2/5 - y$, $-z$.

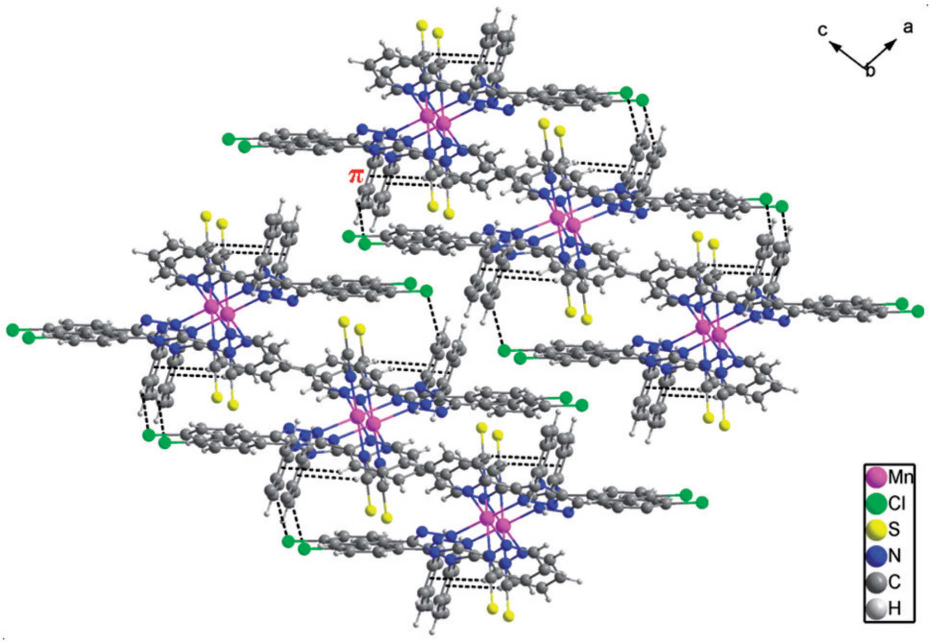

Figure 2. The crystal packing of **1** viewed along the *b*-axis showing hydrogen bonding.

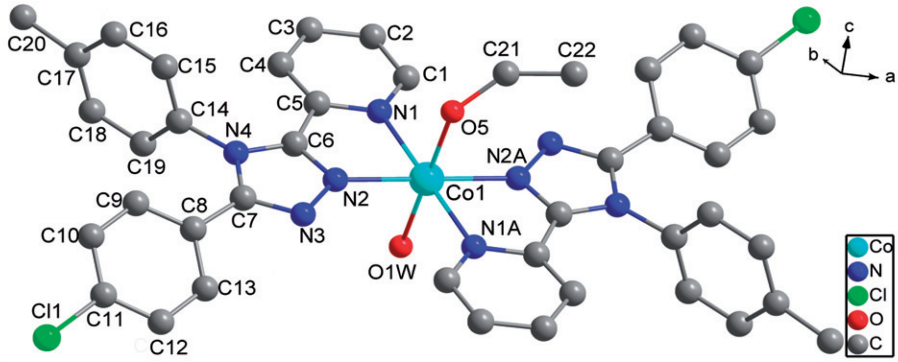

Figure 3. Projection of the structure of **2** with the atomic labeling system. Hydrogens, lattice H_2O, and ClO_4^- are omitted for clarity.

coordinated by four nitrogens from two L and two oxygens from H_2O and EtOH in axial positions to form a distorted octahedral geometry. This is different from two similar complexes, $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ [MBPT = 4-(*p*-methylphenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole] [22] and *trans*-$[CuL'_2(ClO_4)_2]$ [L′ = 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole] [15], where the axial ligands are H_2O and ClO_4^-, respectively. The ClO_4^- in **2** are uncoordinated. Selected bond lengths and angles for **2** are listed in table 2. Although the bond lengths and angles in **2** are in the normal range, the Co–O distance is 0.054 Å longer than that in $[Co(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$. The coordination mode of L in **2** is similar to that found in **1** and also non-planar. The triazole ring makes dihedral angles of 2.9(3)°, 27.4(3)°, and 87.4(3)° with the pyridyl ring, *p*-chlorophenyl ring and *p*-methylphenyl ring, respectively. The smaller dihedral angle [2.9(3)°] between triazole ring and the pyridyl ring indicates that their co-plane in **2** is much better than that in **1** [11.2(3)°].

There are many intermolecular and intramolecular hydrogen bonds and π–π stacking interactions in the structure of **2** (table 4), associated with closer crystal packing. These hydrogen-bond interactions include: (1) between pyridyl ring and triazole ring [$C1–H1A \cdots N3^a$]; (2) between *p*-methylphenyl ring and ClO_4^- anion [$C20–H20C \cdots O1^b$, $C15–H15A \cdots O1^c$, $C19–H19A \cdots O3^d$]; (3) between ethanol and ClO_4^- anion [$C22–H22C \cdots O2^d$]; (4) between *p*-chlorophenyl ring and ClO_4^- [$C13–H13A \cdots O3^e$]; (5) between pyridyl ring and ClO_4^- [$C3–H3A \cdots O4^b$]. Similar to **1**, there is an intramolecular edge-to-face $C–H \cdots \pi$ interaction involving C4–H4 and *p*-methylphenyl ring ($H4 \cdots \pi = 2.710$ Å and $\angle C4–H4 \cdots \pi = 154°$) (figure 4). Notably, a strong offset face-to-face π–π interaction exists between two parallel pyridyl rings with a plane–plane distance of 3.625 Å and a centroid–centroid distance of 3.903 Å (figure 5). These extensive hydrogen bonds and π–π stacking interactions assemble the cation units, ClO_4^- anions, and lattice water into a 3-D structure.

3.4. *IR spectrum*

The IR spectrum of free L shows medium bands at 1585 and 1567 cm^{-1}, attributable to the pyridyl ring vibrations. Upon pyridine coordination to a metal, the higher band is

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

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
C1–H1A···N3^{a}	0.930	2.580	3.389(6)	145
C20–H20C···O1^{b}	0.960	2.706	3.529(3)	144
C15–H15A···O1^{c}	0.930	2.696	3.555(6)	154
C22–H22C···O2^{d}	0.960	2.260	3.017(6)	135
C13–H13A···O3^{e}	0.930	2.783	3.494(6)	134
C19–H19A···O3^{d}	0.930	2.604	3.387(5)	142
C3–H3A···O4^{b}	0.930	2.695	3.512(5)	147
C4–H4A···π (C14–19)	0.930	2.710	3.568(6)	154
π–π interaction	Cent···cent	$\pi \cdots \pi$	–	Dihedral angle
π (py)···π (py)^{f}	3.903	3.625	–	0

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

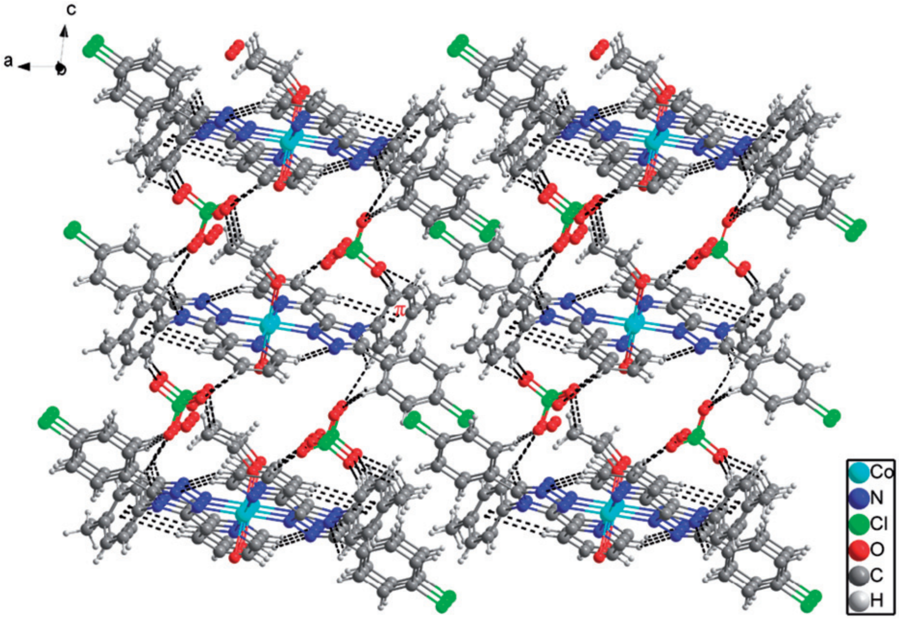

Figure 4. The crystal packing of **2** viewed along the *b*-axis showing hydrogen bonding.

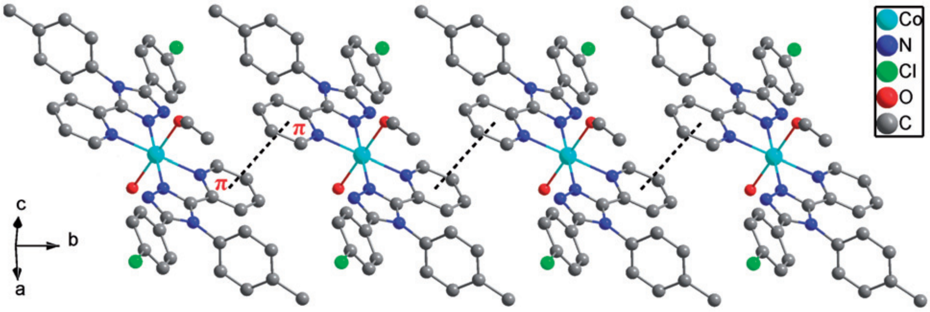

Figure 5. View of two offset face-to-face π–π stacking interactions for two parallel pyridine rings in **2**. Hydrogens have been omitted for clarity.

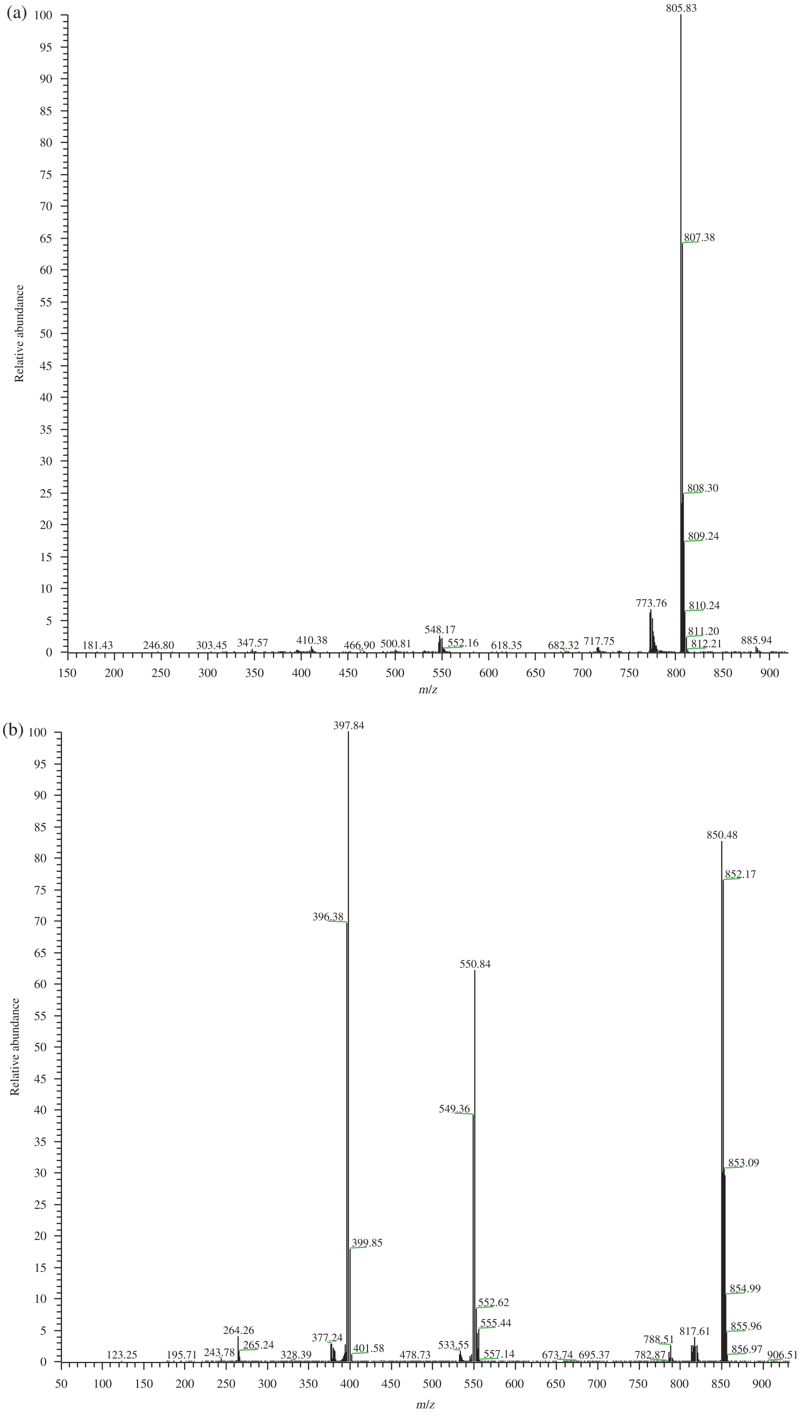

Figure 6. Positive ion ESI-MS of (a) **1** and (b) **2** in methanol solution.

shifted by about 15 wavenumbers [22]. So in the spectrum of **1** (or **2**), a band at 1599 (or 1604) (m) and 1577 (or 1576) cm^{-1} (m) can be assigned to the coordinated pyridyl ring. This means that in **1** and **2** each L uses one pyridyl nitrogen and one triazole nitrogen for chelate binding. In **1**, a very strong band at 2064 cm^{-1} is assigned to C≡N stretching vibrations of two *trans*-oriented thiocyanate groups [20]. In **2**, the bands due to perchlorate are at 1093 (vs), 930 (w), 625 cm^{-1} (s), which can be assigned as the IR-allowed ν mode, IR-forbidden ν mode, and the non-degenerate ClO_3 symmetrical bending frequency, respectively [15]. The medium and broad band centered at 3431 cm^{-1} for **2** is mainly attributed to O–H stretching vibrations of water and ethanol, suggesting the existence of hydrogen-bonding interactions [23]. These features are in agreement with the results of X-ray crystallography. In addition, the stretching vibrations of C(Ph)–Cl bond at 1092, 1090, and 1030 cm^{-1} are attributed to L, **1**, and **2**, respectively.

3.5. *Electrospray ionization-mass spectrometry*

The structures of **1** and **2** in solution were also studied by ESI-MS [24–26]. Figure 6(a) displays the positive ESI mass spectrum of **1** in methanol solution. The base peak at m/z 805.83 is $[MnL_2(NCS)]^+$. Figure 6(b) displays the positive ESI mass spectrum of **2** in methanol. Four main peaks were observed. The peak at m/z 850.48 is $[CoL_2(ClO_4)]^+$. The peak at m/z 550.84 is $[CoL_3]^{2+}$. The peaks at m/z 397.84 and 377.24 are $[CoL_2(EtOH)]^{2+}$ and $[CoL_2]^{2+}$, respectively.

4. Conclusion

New Mn(II) and Co(II) complexes with 3-(*p*-chlorophenyl)-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (L), *trans*-$[MnL_2(NCS)_2]$ (**1**) and *trans*-$[CoL_2(H_2O)(EtOH)](ClO_4)_2 \cdot H_2O$ (**2**) have been synthesized and their molecular structures were determined by X-ray crystallography, IR, and ESI-MS. Structural analyses indicate that two complexes have a similar distorted octahedral core. In **1**, two *trans*-oriented NCS^- coordinate to Mn(II), while two different molecules (H_2O and EtOH) coordinate axially to Co(II) in **2**.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 784877 (**1**) and 784878 (**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 CB21EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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