Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Abnormal conformation change of an asymmetrical triaryltriazole before and after its coordination

Guo-Ping Shen^a, Jian Zhao^a, Jing-Jing Jiang^a, Qin Liu^b, Xuan Shen^a, Yan Xu^a, Dun-Ru Zhu^{a,*}, Xiao-Qin Liu^{a,*}

^a College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China ^b Department of Applied Chemistry, Nanjing University of Finance & Economics, Nanjing 210003, PR China

ARTICLE INFO

Article history: Received 2 June 2011 Received in revised form 6 July 2011 Accepted 9 July 2011 Available online 20 July 2011

Keywords: Syntheses Triazole Crystal structures Complexes Conformation change

ABSTRACT

A new asymmetrical substituted triaryltriazole ligand, 3-(p-methoxyphenyl)-4-(p-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L) and its complexes,*trans*-[MnL₂(NCS)₂] (1) and*trans* $-[CuL₂(ClO₄)₂] (2), have been successfully synthesized and characterized by UV, IR, ESI-MS, elemental analyses and single-crystal X-ray diffraction methods. In the structure, two L ligands are mainly stabilized by two kinds of intermolecular <math>\pi \cdots \pi$ interactions. In the complexes, each L ligand involves a chelating bidentate coordination mode *via* N atom of pyridyl group and one N atom of the triazole. Both complexes show a distorted octahedron containing two *trans*-coordinated anions in 1 with NCS⁻ but in 2 with ClO₄⁻. The dihedral angle between the pyridyl and triazole ring in the free L ligand, 1 and 2 is $0.8(2)^\circ$, $12.8(2)^\circ$ and $9.3(2)^\circ$, respectively, which represents the first example that the triazole–pyridyl twist angle in the complexes of any triaryltriazole is larger than that in the free L ligand.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

During the past two decades, triaryltriazoles ligands have attracted considerable attention in coordination chemistry due to their possessing rich and versatile coordination modes [1] and interesting spin-crossover properties in their iron(II) complexes [2,3]. All kinds of mononuclear [1], dinuclear [4,5] and trinuclear metal complexes [6] with triaryltriazoles ligands have been reported to date. Generally, in the free triaryltriazole, the three aryl rings are not coplanar with the central triazole ring. The X-ray crystal structure analyses of the free triaryltriazoles revealed that the dihedral angles between the pyridyl and triazole ring in all cases are in the range of 16.3(3)-50.1(3)° (Table 3) [1,7-19]. In the complexes of any triaryltriazole, however, the triazole-pyridyl twist angle becomes always smaller in favor of coordination (Table 4) [2–4,6,19–23]. Herein we report a very unusual example that conformation change of a new asymmetrical 3,4,5-tri-substituted triaryltriazole, 3-(p-methoxyphenyl)-4-(p-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L), is abnormal before and after its coordination, that is, the pyridyl and triazole ring is almost in a plane in the free L ligand but is not in its two mononuclear complexes, trans- $[MnL_2(NCS)_2]$ (1) and trans- $[CuL_2(ClO_4)_2]$ (2). The single crystal structures and spectral properties of L, 1 and 2 have been systematically studied.

2. Experimental section

2.1. Materials and measurements

Melting points were determined using an X4 digital microscopic melting point apparatus and are uncorrected. Elemental analyses for M²⁺ (M = Mn, 1; Cu, 2) were performed on a Zeeman inductively coupled plasma (ICP) spectrometer, while the C, H, N analyses were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. FT-IR spectra were recorded on a Nicolet 380 FT-IR instrument using KBr disks in the range of 4000-400 cm⁻¹. UV-vis spectra were recorded on a Perkin-Elmer Lambda 35 spectrometer at r.t. in acetonitrile solution. ¹H NMR spectra were measured on a Bruker AM 500 MHz spectrometer at ambient temperature in CDCl₃. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Electrospray ionization mass spectrum (ESI-MS) was recorded with a Finnigan mat APISSQ 710 mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 cm³ min⁻¹. The spray voltage was 4.5 kV and the capillary voltage was 28.7 V. The capillary temperature was 200 °C. All chemicals used were of analytical grade, and solvents were purified by conventional methods.

2.2. Synthesis of L

The ligand, 3-(*p*-methoxyphenyl)-4-(*p*-bromophenyl)-5-(2pyridyl)-1,2,4-triazole (L) was prepared by condensation of



^{*} Corresponding authors. Tel.: +86 25 83587717; fax: +86 25 83172261. *E-mail address:* zhudr@njut.edu.cn (D.-R. Zhu).

^{0022-2860/\$ -} see front matter \odot 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2011.07.017

Compounds	L	1	2
Empirical formula	C ₂₀ H ₁₅ BrN ₄ O	$C_{42}H_{30}Br_2MnN_{10}O_2S_2$	$C_{40}H_{30}Br_2Cl_2CuN_8O_{10}$
Formula weight	407.27	985.64	1076.98
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
a (Å)	13.934(3)	14.518(3)	8.9069(12)
b (Å)	11.277(2)	9.1784(16)	30.698(4)
c (Å)	22.920(5)	16.189(3)	8.1360(10)
β (°)	93.558(3)	101.503(2)	108.797(2)
V (Å ³)	3594.6(13)	2114.0(6)	2105.9(5)
Ζ	8	2	2
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.505	1.548	1.698
$\mu ({\rm mm}^{-1})$	2.304	2.351	2.611
F (0 0 0)	1648	990	1078
Crystal size (mm)	$0.16 \times 0.14 \times 0.08$	$0.26 \times 0.16 \times 0.12$	$0.24 \times 0.14 \times 0.10$
θ range	1.78-25.50	1.43-26.00	1.33-25.50
Reflections collected	11,048	13,315	15,269
Independent reflections	3331 [<i>R</i> _{int} = 0.0298]	$4085 [R_{int} = 0.0619]$	3901 [R _{int} = 0.0521]
Data/restraints/parameters	3331/0/235	4085/0/268	3901/174/325
Goodness-of-fit on F^2	1.041	0.962	1.029
$R/wR [I > 2\sigma(I)]$	0.0348/0.0914	0.0455/0.0962	0.0452/0.1095
<i>R/w</i> R (all data)	0.0629/0.1103	0.1134/0.1151	0.0885/0.1307
Max., Min. $\Delta \rho$ (e Å ⁻³)	0.248, -0.372	0.525, -0.556	0.637, -0.351

 Table 1

 Crystal data and structure refinement for L, 1 and 2.

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

L		1		2	
N1-C1	1.343(4)	Mn1–N1	2.256(3)	Cu1–N1	2.052(3)
N1-C5	1.313(4)	Mn1–N2	2.220(3)	Cu1–N2	1.966(2)
		Mn1–N5	2.173(4)	Cu1-05	2.434(3)
N2-N3	1.387(4)	N2-N3	1.374(4)	N2-N3	1.373(3)
01–C14	1.425(4)	01–C14	1.400(5)	01–C14	1.421(4)
Br1-C18	1.898(3)	Br1–C18	1.894(4)	Br1–C18	1.888(3)
		N5-C21	1.154(5)		
		S1-C21	1.620(5)		
C1-N1-C5	116.4(3)	N1-Mn1-N2	73.2(2)	05-Cu1-N1	88.1(2)
N3-N2-C6	108.3(2)	N1-Mn1-N5	88.6(2)	05-Cu1-N2	91.6(2)
C6-N4-C7	105.5(2)	N2-Mn1-N5	91.7(2)	N1-Cu1-N2	80.0(1)
		N5-C21-S1	178.7(4)		
01–C11–C12	125.0(3)	Mn1-N5-C21	166.2(4)	Cu1-05-Cl1	135.6(3)
C11-01-C14	118.2(2)	C11-01-C14	117.7(4)	C11-01-C14	117.6(3)

4,4'-dibromophenylphosphazoanilide (1.786 g, 4.8 mmol) with *N*-(*p*-methoxyphenylcarbonyl)-*N*'-(2-pyridylcarbonyl)hydrazine (1.085 g, 4.0 mmol) in *o*-dichlorobenzene at 190 °C for 5 h [11], yield 0.982 g (60%), m.p. 219–222 °C. Single crystals of the **L** ligand suitable for X-ray diffraction study were obtained from anhydrous ethanol upon slow evaporation at ambient temperature. Elemental analyses: found (%): C, 58.79; H, 3.66; N, 13.83. C₂₀H₁₅BrN₄O Calcd. (%): C, 58.98; H, 3.71; N, 13.76. UV (nm): λ = 228, 281. IR (cm⁻¹): ν = 3058.9(w), 2958.5(w), 2835.5(w), 1613.7(m), 1587.3(m), 1567.1(m), 1493.5(s), 1474.6(s), 1282.1(s), 1067.5(m), 1029.1(s), 999.4(m). ¹H NMR δ : 3.80 (s, 3H), 6.82–6.85 (d, 2H), 7.09–7.13 (d, 2H), 7.21–7.23 (t, 1H), 7.35–7.38 (d, 2H), 7.50–7.56 (d, 2H), 7.74–7.77 (t, 1H), 8.16–8.18 (d, 1H), 8.32–8.33 (d, 1H). ESI-MS: *m/z* = 409.2.

2.3. Synthesis of trans-[MnL₂(NCS)₂] (1)

A solution of $MnCl_2 \cdot 6H_2O$ (0.040 g, 0.20 mmol) and anhydrous ethanol (5 cm³) was added dropwise to a stirring solution of L (0.163 g, 0.40 mmol) in boiling anhydrous ethanol (10 cm³). The resulting solution was mixed with an EtOH solution containing KSCN (0.039 g, 0.40 mmol). The light-yellow powder that formed

was isolated, washed with H₂O and EtOH, and dried in vacuo to yield 0.165 g (83.7%) of the complex. The light-yellow single crystals suitable for X-ray diffraction were obtained by evaporation from an ethanol solution. Elemental analyses: found (%): Mn, 5.95; C, 51.27; H, 2.83; N, 13.91. C₄₂H₃₀Br₂MnN₁₀O₂S₂ Calcd. (%): Mn, 5.57; C, 51.18; H, 3.07; N, 14.21. UV (nm): λ = 313, 332. IR (cm⁻¹): ν = 3070.8(w), 2967.8(w), 2066.8(vs), 1611.3(m), 1600.3(m), 1578.8(m), 1489.8(s), 1250.2(s), 1067.6(m), 1023.8(m), 845.2(m), 637.4(w). ESI-MS: *m/z* = 927.58, 837.25, 431.42.

2.4. Synthesis of trans- $[CuL_2(ClO_4)_2]$ (2)

Complex **2** was obtained in a yield of 91.2% by a procedure similar to complex **1** but using Cu(NO₃)₂·3H₂O and NaClO₄·H₂O instead of MnCl₂·6H₂O and KSCN, respectively. Blue single crystals suitable for X-ray analysis were obtained from ethanol upon slow evaporation. Elemental analyses: found (%): Cu, 6.25; C, 44.68; H, 2.63; N, 10.19. C₄₀H₃₀Br₂Cl₂CuN₈O₁₀ Calcd. (%): Cu, 5.90; C, 44.61; H, 2.81; N, 10.40. UV (nm): λ = 319, 338, 647. IR (cm⁻¹): ν = 3081.8(w), 2975.6(w), 1611.5(m), 1604.5(m), 1582.5(m), 1501.0(s), 1261.2(m), 1109.2(s), 1067.4(s), 1022.2(m), 926.7(w), 622.4(m). ESI-MS: *m*/*z* = 915.00, 837.17, 642.92, 431.33.

Table 3Triazole-pyridyl twist angle (°) for the known triaryltriazoles.

Structure	La	R ₁	R ₂	R ₃	R ₄	Х	Py/Trz	Reference
R ₂	L	OCH ₃	Br	Н	Н	Н	0.8(2)	This work
	L^1	CH_3	OCH ₃	Н	Н	Н	46.2(2)	[7]
$R_4 \times X$	L ²	Cl	OCH ₃	Н	Н	Н	35.1(1)	[8]
Υ	L3	Н	Н	CH_3	Н	Н	36.0(2)	[9]
	L^4		CH ₃	Н	Н	Н	28.1(2)	[10]
Ý	L ⁵	Cl	CH ₃	Н	Н	Н	No data	[20]
Ń.	L ₆	OCH ₃	Cl	Н	Н	Н	23.7(2)	[11]
$\langle \rangle \rightarrow R_1$	L ⁷	CH_3	Cl	Н	Н	Н	43.4(1)	[12]
	L ⁸	Cl	Cl	Н	Н	Н	18.5(3)	[11]
	L9	Br	Cl	Н	Н	Н	16.3(3)	[11]
	L ¹⁰	Н	Н	Н	Н	Ν	No data	[21]
R ₂	L ¹¹	Н	i-Pr	Н	Н	Н	29.8(2), 43.7(2)	[13]
	L ¹²	Н	t-Bu	Н	Н	Н	25.0(3), 33.3(3)	[14]
R_4 X R_3	L ¹³	Н	OCH ₃	Н	Н	Н	26.9(1), 47.9(1)	[1]
\uparrow \uparrow	L ¹⁴	Н	OEt	Н	Н	Н	20.1(1), 30.0(1)	[15]
L _	L ¹⁵	Н	CH ₃	Н	Н	Н	32.0(3), 48.0(3)	[16]
\checkmark	L ¹⁶	Н	Н	CH ₃	Н	Н	35.9(3), 36.8(3)	[17]
Ń.	L ¹⁷	Н	CH ₃	CH ₃	Н	Н	36.5(2), 50.1(3)	[18]
$\langle \rangle \to R_1$	L ¹⁸	Н	Н	Н	Н	Н	30.1(2), 32.7(2)	[1]
$\sim N$ N-N N-	L ¹⁹	Н	Н	Н	Н	Ν	No data	[19]
	L ²⁰	Н	Cl	Н	Н	Н	26.9(1), 28.7(1)	[1]
	L ²¹	Н	Br	Н	Н	Н	28.1(2), 46.8(2)	[1]
	L ²²	Н	Н	Cl	Cl	Н	No data	[19]
	L ²³	Н					No data	[19]

^a $L^4 = 3-(4-pyridyl)-4-(p-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole; L^{23} = 4-pyrrolyl-3,5-di(2-pyridyl)-1,2,4-triazole.$

Table 4

Triazol	le-pyridyl	twist	angle	(°)	for	comp	olexes	of	any	triary	ltriazol	les
			· · · ·									

Complexes	Py/Trz	Reference
$[MnL_2(NCS)_2]/[CuL_2(ClO_4)_2]$	12.8(2)/9.3(2)	This work
[MnL5 ₂ (NCS) ₂]/	11.2(3)/2.9(3)	[20]
$[CoL_{2}^{5}(H_{2}O)(EtOH)](ClO_{4})_{2}\cdot H_{2}O$		
$[MnL_{2}^{6}(NCS)_{2}]$	13.2(1)	Our work ^a
[FeL ⁸ ₂ (NCSe) ₂]	11.1(2)	Our work ^a
[FeL ⁹ ₂ (NCS) ₂]	10.3(3)	Our work ^a
[CuL ¹⁰ ₂ (ClO ₄) ₂]·MeCN	5.9(2)	[21]
$[FeL^{11}_{2}(NCS)_{2}]$	10.6(3),	Our work ^a
	35.2(3)	
[Ni ₂ L ¹³ ₂ Cl ₂ (H ₂ O) ₂]Cl ₂ ·7H ₂ O	2.2(2), 3.4(2)	[4]
$[FeL^{15}_{2}(NCS)_{2}]$	11.6(3),	[3]
	14.8(3)	
$[FeL^{16}_{2}(NCS)_{2}]$	16.7(2),	[3]
	33.9(2)	
$[Fe_3L^{18}_4(NCS)_6]$	19.6(1)-31.5(1)	[6]
$[FeL^{19}_{3}](BF_{4})_{2} \cdot 3.6 MeCN \cdot Et_{2}O$	4.3(2)-45.4(1)	[19]
$[FeL^{20}_{3}(NCS)_{2}]$	12.5(2),	Our work ^a
	15.5(2)	
$[CoL^{21}_{2}(NCS)_{2}]$	9.4(8), 13.5(8)	[22]
[FeL ²² ₃](BF ₄) ₂ ·MeCN·Et ₂ O	4.0(2)-30.0(2)	[19]
$[CoL^{23}_{2}(DMF)_{2}](ClO_{4})_{2}$	6.1(2), 24.7(2)	[23]
$[Co_2L^{23}_2(DMF)_2(H_2O)_2](ClO_4)_4 \cdot 0.5Et_2O$	6.7(4), 10.4(3)	[23]

^a Unpublished results.

2.5. X-ray data collection and structure determination

The well-shaped single crystals of **L**, **1** and **2** were selected for Xray 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 8 s using a graphite-monochromated Mo K α (λ = 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 [24]. All non-hydrogen atoms were anisotropically refined. Atoms 02, 03, 04 and 05 of one ClO₄⁻ anion in **2** were found to be highly disordered with an occupancy of 0.807(3) for 02, 03, 04 and 05, and 0.193(3) for 02A, 03A, 04A and 05A, respectively. All H atoms



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

were located from a difference map and refined isotropically. Crystallographic data are summarized in Table 1. The selected bond lengths and angles for L, 1 and 2 are listed in Table 2. CCDC for L, 1 and 2 are 822,798, 822,799, 822,800, respectively.

Table 5
The hydrogen bonding geometry and π - π stacking interactions of L

D—H· · ·A	D—H (Å)	H···A (Å)	$D{\cdots}A~({\AA})$	D—H···A (°)
C3-H3A···N2 ^a C13-H13A···N3 ^b C14-H14C·· π π ·· π interaction π (trz)·· π (trz) ^c π (py)·· π (py) ^c	0.93 0.93 0.96 centcent 3.632 3.751	2.56 2.56 3.04	3.446(4) 3.431(4) 3.568(4)	159 156 116 Dihedral angle 0.86 1.98

^a Symmetry codes: 3/2 - x, 1/2 + y, -1/2 - z.

^b Symmetry codes: 1 - x, y, -1/2 - z.

^c Symmetry codes: 1 - x, y, 3/2 - z.



Fig. 2. The crystal packing of L showing the hydrogen bonding and π stacking interactions.

3. Results and discussion

3.1. Syntheses

The asymmetrical 3,4,5-triaryl-substituted 1,2,4-triazole ligand (**L**) reacts with M^{2+} (M = Mn and Cu) ion and the anion (NCS⁻ and ClO₄⁻) in molar ratio 2:1:2 to obtain two neutral mononuclear hexacoordinate complexes, *trans*-[MnL₂(NCS)₂] (**1**) and *trans*-[CuL₂(ClO₄)₂] (**2**), which are stable in air. Yields of complexes **1** and **2** are 83.7% and 91.2%, respectively. The elemental analyses were satisfactory and indicate that each complex contains one metal ion, two triaryltriazole ligands, and two coordinated anions (**1**: NCS⁻, **2**: ClO₄⁻).

3.2. Crystal structure of L

A perspective view of **L** with the atom-numbering scheme is shown in Fig. 1. Both bond lengths and angles in **L** are comparable with those reported for the related structures [1,7-19]. The X-ray structure analysis indicates that **L** consists of two substituted

Table 6 The hydrogen bonding geometry and π - π stacking interactions of **1**.

D—H···A	D—H (Å)	H···A (Å)	D· · ·A (Å)	D−H···A (°)
C3-H3A···S1 ^a	0.93	2.836	3.559(5)	135
C14-H14B···S1 ^b	0.96	2.863	3.555(5)	130
C20-H20A···O1 ^c	0.93	2.692	3.484(4)	143
C4-H4A··· π	0.93	2.942	3.769(5)	149

^a Symmetry codes: x, y - 1, z.

^b Symmetry codes: 1 - x, 2 - y, -z.

^c Symmetry codes: x, 1.5 - y, 0.5 + z.

phenyl rings, one pyridyl group and one triazole ring. The pyridyl and triazole ring is almost in a plane with a dihedral angle of 0.8(2)°, which has not been observed in all the free triaryltriazole ligands [1,7-19] (Table 3). The central 1,2,4-triazole ring is oriented at dihedral angles of 89.4(1)° and 86.9(2)° with respect to the *p*-methoxyphenyl ring and the *p*-bromophenyl ring, respectively. It is noticeable that two L ligands are mainly stabilized by two kinds of intermolecular $\pi \cdots \pi$ interactions. One strong offset face-to-face $\pi \cdots \pi$ interaction exists between two central triazole rings containing N4 and N4^c (1 - x, y, 3/2 - z), respectively, with a centroid-centroid distance of 3.632 Å and a dihedral angle of 0.86°. Another $\pi \cdots \pi$ interaction exists between two neighboring pyridyl rings containing N1 and N1^c (1 - x, y, 3/2 - z), respectively, with a centroid–centroid distance of 3.751 Å and a dihedral angle of 1.98°. In addition, there are also one C–H $\cdots\pi$ interaction and two C—H \cdots N hydrogen bonds in the L ligand (Table 5 and Fig. 2). We think that it is these intermolecular and intramolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions that determine the dihedral angle of the pyridyl and triazole ring.

3.3. Crystal structure of 1

A projection of the structure of **1** is presented in Fig. 3, together with the atomic labeling system. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ and there is an inversion center at the Mn(II) atom. Each Mn(II) atom adopts a distorted [MnN₆] octahedral geometry coordinated by four nitrogen atoms from two L ligands in the equatorial plane and two nitrogen atoms from two NCS⁻ ions in the axial positions. This feature is also different from that found in a mononuclear Mn(II) complex with asymmetrical 3,5-disubstituted 1,2,4-triazole, *cis*-[MnL'₂(NCS)₂] [25] [L' = 3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole] where the two NCS⁻ anions are in the *cis* arrangement. Each L ligand coordinates to Mn(II) atom *via* N1 atom of the pyridyl ring and N2 atom of the triazole, which is similar to the coordination modes in the related Mn(II) complexes [20,26–27]. The Mn–N



Fig. 3. Projection of the structure of 1 with the atomic labeling system. Hydrogen atoms are omitted for clarity.



Fig. 4. The crystal packing of 1 viewed along the *b*-axis showing the hydrogen bonding.



Fig. 5. Projection of the structure of 2 with the atomic labeling system. Hydrogen atoms are omitted for clarity.

Table 7						
The hydrogen	bonding	geometry	and $\pi - \pi$	stacking	interactions	of 2 .

D—H···A	D—H (Å)	H· · ·A (Å)	$D{\cdots}A~({\mathring{A}})$	D—H···A (°)
C1—H1A···N3 ^a	0.93	2.31	3.117(4)	144
C2−H2A···O2 ^b	0.93	2.59	3.373(5)	143
C3—H3A· · · O5 ^c	0.93	2.55	3.166(4)	124
C4—H4A···O3A ^c	0.93	2.72	3.427(1)	134
C12−H12A····O4 ^d	0.93	2.67	3.526(5)	154
C14−H14B····O1 ^e	0.96	2.74	3.673(5)	164
C16−H16A····O2 ^f	0.93	2.79	3.614(5)	148
C4—H4A·…π	0.93	3.07	3.886(3)	147
C9—H9A…π	0.93	2.82	3.601(5)	142
$\pi \cdots \pi$ interaction	cent⊷cent	$\pi \cdots \pi$		Dihedral angle
$\pi (py) \cdots \pi (py)^{g}$	4.139	3.694		0.0

^a Symmetry codes: 2 - x, -y, 2 - z.

^b Symmetry codes: 3 - x, -y, 2 - z.

^c Symmetry codes: x, y, z - 1.

Symmetry codes: x - 1, y, z.

^e Symmetry codes: *x*, 1/2 - y, $z - \frac{1}{2}$.

^f Symmetry codes: x - 1, y, z - 1.

^g Symmetry codes: -x, -y, 1 - z.

bond lengths are within the normal ranges observed for the octahedral Mn(II) complexes [20,26]. However, the Mn-N_{trz} bond length is 0.036 Å shorter than $Mn{-}N_{py}$ one. The same feature has been observed in the analogous Mn(II) complexes with trans-NCS⁻ groups [20,26]. The NCS⁻ groups are almost linear [N5-C21-S1 178.7(4)°], whereas the Mn-NC(S) linkages are a little bent [Mn1–N5–C21 166.2(4)°]. The L ligand in 1 is non-planar. The triazole ring makes dihedral angles of 12.8(2)°, 50.3(2)° and 75.4(2)° with the pyridyl ring, p-methoxyphenyl ring and p-bromophenyl ring, respectively. It is noticeable that on coordination, the triazole-pyridyl twist angle becomes larger than that observed in the free L ligand. This phenomenon has not been observed in the complexes with triaryltriazole ligands [2-4,6, 19–23] (Table 4). Due to existence of a dihedral angle $(76.8(2)^{\circ})$ between the pyridyl ring and the *p*-bromophenyl ring in the L ligand, there is an intramolecular edge-to-face C–H $\cdots\pi$ interaction involving C4–H4A and the *p*-bromophenyl ring (H4A··· π = 2.942 Å and C4—H4A··· π = 149°). The crystal structure is further stabilized by weak intermolecular C-H···S and C-H···O hydrogen bonds (Table 6 and Fig. 4). These intramolecular and



Fig. 6. The crystal packing of 2 viewed along the *a*-axis showing the hydrogen bonding.



Fig. 7. View of one offset face-to-face $\pi \cdots \pi$ stacking interaction for two parallel pyridyl rings and two edge-to-face C-H $\cdots \pi$ stacking interactions for *p*-bromophenyl ring in **2**.

intermolecular interactions may result in the larger dihedral angle of the pyridyl and triazole ring in **1**.

3.4. Crystal structure of 2

Fig. 5 presents the structure of **2** with its atom numbering system. The crystal structure consists of a $[CuL_2]^{2+}$ cation and two ClO_4^- anions. The Cu(II) atom in **2** is also in a distorted octahedral geometry coordinated by four nitrogen atoms from two **L** ligands and two oxygen atoms from two ClO_4^- anions. The Cu–N bond lengths are within the normal ranges observed for a octahedral Cu(II) complex [28]. However, the Cu–N_{trz} bond length is 0.085 Å shorter than Cu–N_{py}. The same feature has been observed in the similar Cu(II) complexes

[29,30]. The Cu–O distance is 2.435(3) Å, indicating the involvement of two ClO_4^- ions in the coordination [31], which is similar to that found in *trans*-[CuL'₂(ClO₄)₂] [28]. The coordination mode of **L** ligand in **2** is similar to that found in **1** and the **L** ligand is also non-planar. The triazole ring makes dihedral angles of 9.3(2)°, 25.2(2)° and 74.2(2)° with the pryidyl ring, *p*-methoxyphenyl ring and *p*-bromophenyl ring, respectively. Once again, the triazole-pyridyl twist angle of the triaryltriazole in **2** is larger than that observed in the free **L** ligand. This abnormal conformation change may due to the existence of intermolecular and intramolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions in **2** (*vide infra*).

There are five kinds of intermolecular and intramolecular hydrogen bond interactions in the structure of **2** (Table 7), which is significantly associated with the closer crystal packing. These



Fig. 8. IR spectra of L, 1 and 2 in the region of characteristic bands of pyridyl ring (1650–1550 $\rm cm^{-1}).$

hydrogen bond interactions include: (1) between pyridyl ring and triazole ring [C1–H1A···N3^a]; (2) between two methoxy groups [C14–H14A···O1^e]; (3) between pyridyl ring and ClO_4^- anion [C2–H2A···O2^b, C3–H3A···O5^c, C4–H4A···O3A^c]; (4) between *p*-bromophenyl ring and ClO_4^- anion [C16–H16A···O2^f]; (5) between *p*-methoxyphenyl ring and ClO_4^- anion [C12–H12A···O4^d]. Different from **1**, there are two kinds of intramolecular edge-toface C–H··· π interactions in **2** involving C4–H4A and C9–H9A,

respectively, and *p*-bromophenyl ring (H4A··· π = 3.07 Å and C4—H4A··· π = 147°; H9A··· π = 2.82 Å and C9—H9A··· π = 142°) (Fig. 6). Notably, an offset face-to-face π - π interaction exists between two parallel pyridyl rings with a plane-plane distance of 3.694 Å and a centroid-centroid distance of 4.139 Å (Fig. 7). These extensive hydrogen bonds and π - π stacking interactions assemble the cation units and ClO₄⁻ anions into a three-dimensional structure.

3.5. IR spectrum

The IR spectrum of free L shows two medium bands at 1587.3 and 1567.1 cm⁻¹, attributable to the pyridyl ring vibrations. Upon pyridine coordination to a metal the higher band is shifted by about 15 wavenumbers [27]. So in the spectrum of the complex 1 (or 2), a band at 1600.3 (or 1604.5) (m) and 1578.8 (or 1582.5) cm⁻¹ (m) can be assigned to the coordinated pyridyl ring (Fig. 8). This means that in 1 and 2, each L ligand uses one pyridyl nitrogen and one triazole nitrogen for chelate binding. In 1, a very strong band at 2066.8 cm⁻¹ is assigned to C \equiv N stretching vibrations of two trans-oriented thiocyanate groups [4]. In 2, the bands due to the perchlorate anions are around 1109.2 (s), 926.7 (w), 622.4 cm⁻¹ (m), which can be assigned as the IR-allowed v mode, IR-forbidden v mode and the nondegenerate ClO₃ symmetrical bending frequency, respectively [32]. These features are in agreement with the results of X-ray analyses. In addition, the stretching vibrations of C(Ph)—Br bond at 1067.5, 1067.6 and 1067.4 cm^{-1} are attributed to L, 1 and 2, respectively.



Fig. 9. Positive ion ESI-MS of L (a), 1 (b) and 2 (c) in methanol solution.

3.6. UV-vis spectrum

In the UV-vis spectrum of the complex 1 (or 2) in acetonitrile solution, two intense bands at 313 (or 319) and 332 (or 338) nm are attributed to the L π - π^* and n- π^* transitions in contrast to those (228 and 281 nm) in the free L-acetonitrile solution. One band at 647 nm corresponding to the d-d transition is observed for **2**, but no band in the region for **1**.

3.7. Electrospray ionization mass spectrometry (ESI-MS)

The structures of L, 1 and 2 in methanol solution were also studied by electrospray ionization mass spectrometry (ESI-MS) [33-35]. Fig. 9a displays the positive ESI mass spectrum of L and the base peak at m/z 409.2 is $[L + H]^+$ ion. Fig. 9b shows the positive ESI mass spectrum of **1** and the base peak at m/z 927.58 is [MnL₂(NCS)]⁺ ion. Fig. 9c displays the positive ESI mass spectrum of **2** and three main peaks were observed. The base peak at m/z915.00 is $[Cu(L-OCH_3)_2(ClO_4)]^+$ ion. The peaks at m/z 837.17, 642.92 and 431.33 are $[NaL_2]^+$, $[CuL_3]^{2+}$, $[NaL]^+$ ion, respectively. In addition, it should be mentioned that the formation of the different aggregates in the ESI-MS spectra of 2 can be influenced by the concentration of the complex [36].

4. Conclusions

Two new mononuclear complexes with 3-(p-methoxyphenyl)-4-(p-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L), trans-[MnL₂- $(NCS)_2$] (1) and trans- $[CuL_2(ClO_4)_2]$ (2) have been synthesized, and their molecular structures determined by X-ray crystallography, UV, IR and ESI-MS. Structural analyses indicate that it is the first observation that the triazole-pyridyl twist angle of the triaryltriazole in the complexes is larger than that in the free L ligand. This abnormal conformation change is due to the existence of different intermolecular and intramolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions in the crystal structures of the free ligand and its complexes.

Acknowledgments

This work was funded by the National Nature Science Foundation of China (Nos. 20771059, 20971068 and 20976082) and the Natural Science Foundation of Jiangsu Province (BK2008371).

References

- [1] M.H. Klingele, S. Brooker, Coord. Chem. Rev. 241 (2003) 119.
- [2] J.A. Kitchen, S. Brooker, Coord. Chem. Rev. 252 (2008) 2072.
- [3] D. Zhu, Y. Xu, Z. Yu, Z. Guo, H. Sang, T. Liu, X. You, Chem. Mater. 14 (2002) 838. [4] J. Zhou, J. Yang, L. Qi, X. Shen, D. Zhu, Y. Xu, Y. Song, Trans. Metal Chem. 32
- (2007) 711. [5] J.A. Kitchen, A. Noble, C.D. Brand, B. Moubaraki, K.S. Murray, S. Brooker, Inorg. Chem. 47 (2008) 9450.
- [6] J.A. Kitchen, G.N.L. Jameson, V.A. Milway, J.L. Tallon, S. Brooker, Dalton Trans. 39 (2010) 7637.
- [7] S.P. Zhang, Z.D. Liu, S.D. Chen, S. Yang, S.C. Shao, Acta Crystallogr. E62 (2006) 01516.
- [8] Z.D. Liu, S.P. Zhang, Y. Wei, S.C. Shao, Acta Crystallogr, E63 (2007) 04634.
- [9] Z.N. Gong, Z.X. Wang, Y. Liu, Acta Crystallogr. E65 (2009) 03214.
 [10] L.T. Yuan, H. Zhang, Z.X. Wang, Acta Crystallogr. E65 (2009) 01225.
- [11] J. Zhao, G.-P. Shen, Y. Zhang, X. Shen, D.-R. Zhu, J. Heterocycl. Chem. (2011), in press.
- [12] S.P. Zhang, Z.D. Liu, S.C. Shao, Acta Crystallogr. E62 (2006) o1279.
- [13] S.P. Zhang, Z.L. You, S.C. Shao, H.L. Zhu, Acta Crystallogr. E61 (2005) o8.
- [14] S.P. Zhang, H.J. Liu, S.C. Shao, Y. Zhang, D.G. Sun, S. Yang, H.L. Zhu, Acta Crystallogr, E60 (2004) o1113
- [15] S.P. Zhang, Z.D. Liu, S. Yang, X.Y. Qiu, S.C. Shao, Acta Crystallogr. E61 (2005) 03108
- [16] D.-R. Zhu, Y. Song, Y. Xu, Y. Zhang, S.S.S. Raj, H.-K. Fun, X.-Z. You, Polyhedron 19 (2000) 2019.
- [17] S.P. Zhang, Z.L. You, S.C. Shao, H.L. Zhu, Acta Crystallogr. E61 (2005) o27.
- [18] H.J. Liu, S.C. Shao, S.P. Zhang, S. Yang, F.Y. Hao, C.P. Li, H.L. Zhu, Acta Crystallogr. E60 (2004) 0722
- [19] J.A. Kitchen, N.G. White, M. Boyd, B. Mounaraki, K.S. Murray, P.D.W. Boyd, S. Brooker, Inorg. Chem. 48 (2009) 6670.
- [20] J. Zhao, H.-M. Cheng, G.-P. Shen, Y. Xu, D.-R. Zhu, J. Coord. Chem. 64 (2011) 942.
- [21] M.H. Klingele, S. Brooker, Inorg. Chim. Acta 357 (2004) 3413.
- [22] L. Qi, D.-R. Zhu, D.-J. Xie, Y.-F. Wu, X. Shen, Chin. J. Inorg. Chem. 24 (2008) 868. [23] M.H. Klingele, P.D.W. Boyd, B. Moubaraki, K.S. Murray, S. Brooker, Eur. J. Inorg.
- Chem. (2000) 573. [24] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
- [25] J. Zhao, W. Lu, L. Chen, X. Shen, Y. Xu, D.R. Zhu, Chin. J. Inorg. Chem. 27 (2011) 743.
- [26] D.-R. Zhu, T.-W. Wang, S.-L. Zhong, Y. Xu, X.-Z. You, Chin. J. Inorg. Chem. 20 (2004) 508.
- [27] D. Zhu, Y. Xu, Y. Mei, Y. Shi, C. Tu, X. You, J. Mol. Struct. 559 (2001) 119.
- [28] W. Lu, D.-R. Zhu, Y. Xu, H.-M. Cheng, J. Zhao, X. Shen, Struct. Chem. 21 (2010) 237
- [29] Z. Wang, Y. Lan, P. Wu, L. Huang, Acta Crystallogr. E64 (2008) m593.
- [30] Z.X. Wang, X.N. Gong, Z.R. Qu, P.F. Wu, X.M. Zhang, Chin. J. Inorg. Chem. 25 (2009) 567.
- [31] S.H. Rahaman, D. Bose, R. Ghosh, G. Mostafa, H.K. Fun, B.K. Ghosh, Struct. Chem. 18 (2007) 237.
- [32] B.J. Hathaway, A.A.G. Tomlinson, Coord. Chem. Rev. 5 (1970) 1.
- [33] V. Katta, S.K. Chowdhury, B.T. Chait, J. Am. Chem. Soc. 112 (1990) 5348.
- [34] S.R. Wilson, A. Yasmin, Y. Wu, J. Org. Chem. 57 (1992) 6941.
- [35] R. Arakama, T. Matuo, H. Ito, I. Katakuse, K. Nozaki, T. Ohno, M. Haga, Mass Spectrom. 29 (1994) 289.
- [36] Z. Fei, D. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, Eur. J. Inorg. Chem. (2005) 860.