ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 1, pp. 43–47. © Pleiades Publishing, Ltd., 2014.

Structural Diversity of Two Novel Complexes of Co(II) with Bis-Triazole Ligand: From One-Dimensional Chain to Two-Dimensional Porous Network[1]

Y. Y. Liu[a, b, *], P. Yang[a, b], and B. Ding[a, b, *]

[a] *Tianjin Key Laboratory of Structure and Performance for Functional Molecule, College of Chemistry, Tianjin Normal University, Tianjin, 300387 P.R. China*

[b] *Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry (Tianjin Normal University), Ministry of Education, Tianjin, 300387 P.R. China*

**e-mail: liuyuanyuan1973@yahoo.com.cn*

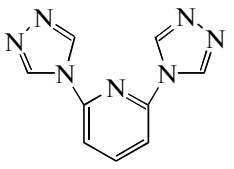
Received July 12, 2012

Abstract—Using two novel bis-triazole ligands, 2,6-bis(1,2,4-triazole-4-yl)pyridine (L^1) and 1,6-bis(1,2,4-triazole-1-yl)hexane (L^2), one novel one-dimensional (1D) chain polymer $[Co(NCS)_2(L^1)_2]_n$ (**I**) and one two-dimensional (2D) coordination polymer $[Co(NCS)_2(L^2)_2]_n$ (**II**) have been synthesized and structurally characterized. The crystal crystallizes in the triclinic system for **I**, space group $P\bar{1}$, $a = 7.879(6)$, $b = 8.830(7)$, $c = 9.837(8)$ Å, $\alpha = 70.230(11)°$, $\beta = 115.474(6)°$, $\gamma = 85.591(12)°$, $Z = 1$. The crystal crystallizes in the mo-noclinic system for **II**, space group $P\bar{1}$, $a = 7.879(6)$, $b = 8.830(7)$, $c = 9.837(8)$ Å, $\alpha = 70.230(11)°$, $\beta = 115.474(6)°$, $\gamma = 85.591(12)°$, $Z = 1$. The structural diversity of these two new Co(II) complexes vary from 1D chain to 2D porous supramolecular network, which may be ascribed to ligand directing effects under similar synthetic conditions (L^1 contains rigid pyridine spacers while L^2 contains flexible hexane spacers).

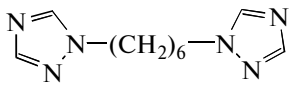
DOI: 10.1134/S1070328414010047

INTRODUCTION

Coordination polymers have aroused much interest as materials owing to potential new electronic, optical, magnetic, and catalytic properties, as well as intriguing structural motifs [1]. A key step for construction of polymeric transition metal complexes is to select appropriate multidentate bridging ligands [2]. Recently, new flexible bispolyazole-type ligands, such as 1- or 4-substituted 1,2,4-triazole rings tethered by an alkyl or rigid aromatic spacer, have been used to obtain a wide variety of polynuclear molecules and linear coordination polymers [3, 4]. 2,6-Bis(1,2,4-triazole-4-yl)pyridine (L^1) and 1,6-bis(1,2,4-triazole-1-yl)hexane (L^2) are excellent synthons for the construction of extended structures with the following distinctive characteristics.



(L^1)



(L^2)

These two ligands can donate four nitrogen atoms in coordinating with metal ions to obtain unexpected structures.

On the other hand, neutral organic ligands containing rigid or flexible spacers, such as 4,4'-bipyridine, 1,2-bis(4'-pyridyl)ethane, 1,2-bis(4-pyridyl)propane and many others, have been used to generate a rich variety of metal-organic architectures with different metal ions by various reaction procedure. The ligands L^1 and L^2 represent another class of N-donor organic linkers for constructing coordination polymers. These ligands can produce architectures quite different from those obtained from pyridyl-based ligands [5]. For these ligands, a variety of zinc(II) and cadmium(II) compounds have been reported [6], while for the Co(II) compounds are less reported.

Recently we reported a series of Zn and Cd complexes with 2,6-bis(1,2,4-triazole-4-yl)ethane exhibiting the anion variations make different supra-molecular structure and the self-assembly of CdN_4O_2 polyhedra from 2D to 1D [7]. As the continuation of this work, using two highly flexible bis-triazole ligands (L^1 contains rigid pyridine spacers while L^2 contains flexible hexane spacers), we isolated a novel 1D single-chain (**I**) and one two-dimensional (**II**) Co(II) compounds. The structural diversity of these two new Co(II) complexes vary from 1D chain to 2D porous supra-molecular network, which should be ascribed to ligand directing effects under similar synthetic conditions.

[1] The article is published in the original.

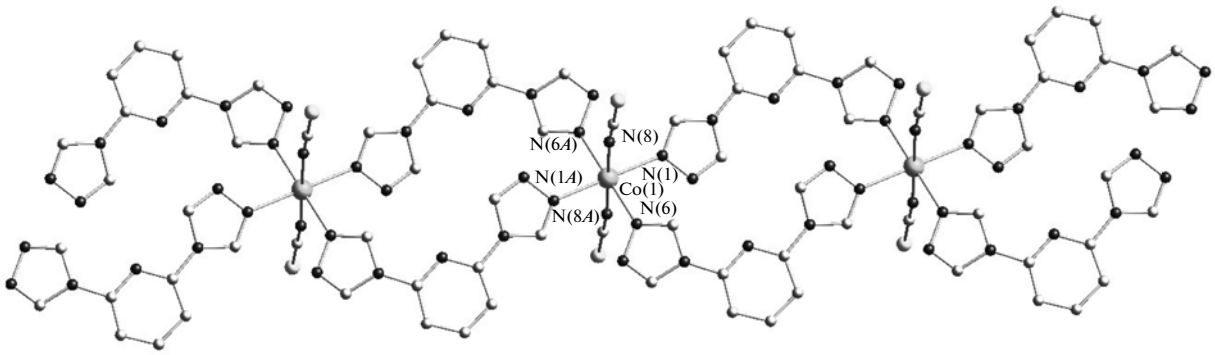


Fig. 1. View of the 1D single chain structure of complex **I**.

EXPERIMENTAL

The triazole ligands L^1 and L^2 were synthesized according to the literature method [8]. All other starting reagents were of A.R. grade and used as purchased. Analyses of C, H, and N were determined on a Perkin-Elmer 240 Elemental analyzer. The FT–IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} range.

Synthesis of $[Co(NCS)_2(L^1)_2]_n$ (I). A ethanol solution (10 mL) of L^1 (2.0 mmol) was added into an aqueous (10 mL) of $CoCl_2 \cdot 6H_2O$ (1.0 mmol) with stirring. The filtrate was refluxed for 1 h. The red crystals of **I** suitable for X-ray diffraction were obtained by evaporation of the filtrate. The yield was 55% (based on Co(II) salts).

For $C_{20}H_{14}N_{16}S_2Co$

anal. calcd., %:	C, 39.94;	H, 2.35;	N, 37.26.
Found, %:	C, 39.98;	H, 2.41;	N, 37.36.

Synthesis of $[Co(NCS)_2(L^2)_2]_n$ (II). A ethanol solution (10 mL) of L^2 (2.0 mmol) was added into an aqueous (10 mL) of $CoCl_2 \cdot 6H_2O$ (1.0 mmol) with stirring. The filtrate was refluxed for 1 h. The red crystals of **II** suitable for X-ray diffraction were obtained by evaporation of the filtrate. The yield was 47% (based on Co(II) salts).

For $C_{22}H_{32}N_{14}S_2Co$

anal. calcd., %:	C, 42.92;	H, 5.24;	N, 31.85.
Found, %:	C, 42.96;	H, 5.38;	N, 31.96.

X-ray crystallography. The data were collected on a Bruker Smart-1000-CCD area detector, all using graphite-monchromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by the direct method and subsequent Fourier difference techniques and refined using a full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97 [9] and SHELXL-97 [10]). Hydrogen atoms were added geometrically and refined with riding model position parameters and fixed isotropic thermal parameters. Crystal data collection and refinement parameters are given in Table 1, the selected bond distances and bond angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 874718 (**I**) and 874715 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structure of **I** exhibits a double-stranded chain. The Co^{2+} ion is in a distorted octahedral arrangement, in which the equatorial plane is formed by four triazole nitrogen atoms and the axial positions are occupied by two *trans*-isothiocyanate ligands (Fig. 1). The Co–N_{NCS} distances (2.069(3) Å) are much shorter than the Co–N^1_L distances (2.201(3) and 2.161(3) Å). The connections between Co^{2+} ions and NCS^- groups are almost linear with a CNCo angle of 172.0(1)°. A dihedral angle of the two triazole rings of 26.6° and Co···Co separation across bridging L^1 ligand is 10.679(6) Å. Two strands of L^1 ligands are wrapped around each other and are held together by Co^{2+} ions, forming a double-stranded chain with 22-membered rings. Because no solvent water molecules are involved into the coordination framework, only non-classical C–H···S and C–H···N interactions stabilize the framework and extend **I** into a 3D supra-molecular architecture (Fig. 2).

Figure 3 shows the asymmetric unit of **II** contains one Co^{2+} cation, four-half of L^2 ligands and two thiocyanate anions. The Co^{2+} ion, which resides at an inversion center, is octahedrally coordinated by two pairs

Table 1. Crystallographic data and experimental details for complexes **I** and **II**

Parameter	Value	
	I	**II**
M	601.52	615.67
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	7.879(6)	9.763(6)
b, Å	8.830(7)	18.112(12)
c, Å	9.837(8)	9.253(6)
α, deg	70.230(11)	90
β, deg	85.591(12)	117.261(9)
γ, deg	65.399(10)	90
V, Å^3	584.0(8)	1454.4(16)
Z	1	2
ρ_{calcd}, g/cm^3	1.699	1.406
$\mu(MoK_\alpha)$, mm^{-1}	0.794	0.773
$F(000)$	303	642
Crystal size, mm	0.16 × 0.12 × 0.10	0.20 × 0.14 × 0.10
Index ranges	$-7 \le h \le 9$,	$-11 \le h \le 11$,
	$-9 \le k \le 10$,	$-21 \le k \le 20$,
	$-9 \le l \le 11$	$-6 \le l \le 11$
Reflections collected/unique	3210/2042	7754/2564
R_{int}	0.0248	0.0913
Reflections with $I > 2\sigma(I)$	1512	1489
GOOF for F^2	1.032	1.068
R index ($I > 2\sigma(I)$)	$R_1 = 0.0384$,	$R_1 = 0.1115$,
	$wR_2 = 0.0829$	$wR_2 = 0.2948$
R index (all data)	$R_1 = 0.0628$,	$R_1 = 0.1616$,
	$wR_2 = 0.0899$	$wR_2 = 0.3269$
Residual electron density (max/min), e Å^{-3}	0.373/–0.273	1.904/–0.720

Table 2. Selected bond distances (Å) and angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Co(1)–N(8)	2.069(3)	Co(1)–N(1)	2.161(3)
Co(1)–N(6)	2.201(3)		
	II		
Co(1)–N(7)	2.118(8)	Co(1)–N(1)	2.132(8)
Co(1)–N(6)	2.162(7)		
Angle	ω, deg	Angle	ω, deg
	I		
N(8)Co(1)N(1)	90.99(12)	N(1)Co(1)N(6)	90.39(10)
N(8)Co(1)N(6)	92.49(10)		
	II		
N(7)Co(1)N(1)	91.2(3)	N(7)Co(1)N(6)	88.4(3)
N(1)Co(1)N(6)	88.7(7)		

of equivalent imine nitrogen atoms from L^2 ligands in the equatorial plane (N(1), N(6), N(6*A*), N(1*A*)) and two equivalent terminal thiocyanate ions occupying the axial positions (N(7) and N(7*A*)). Two triazole rings of the ligand rotate along the C–C single bond axis with the dihedral of 52.1°. The *cis* NCoN bond angles range from 88.4(3)° to 91.2(3)°, and the axial Co–N(7) distances (2.118(8) Å) are similar to the equatorial Co–N(imine) distances (2.132(8) and 2.162(7) Å), indicative of the nearly ideal octahedral environment. Each Co^{2+} ion is linked by four equivalent L^2 ligands to its four neighboring Co^{2+} ions, thus affording 2D (4,4) grid layers parallel to the crystallographic *xy* plane (Fig. 3).

The grid motif has the dimensions of 15.495(5) × 15.495(5) Å (metal-to-metal distances), and the Co···Co···Co corner angles (71.5(3)° and 108.4(7)°) within the motif are close to 90°, suggesting a rhombic geometry. The grid layers are closely stacked in an offset way (Fig. 4) with the cavity of each layer being occupied by the groups from the two neighboring layers, which are generated from the original one by unit translations along the *x* direction. Due to the interdigitation between neighboring layers. The nearest interlayer Co···Co distances are 9.253(6) and 10.169(6) Å between the neighboring layers and between the next-nearest neighboring layers, respectively, both being much shorter than the intralayer one. Further inspection into the structure revealed no classical hydrogen bonds can be observed. Instead, there exist strong C–H–π interactions (C(8)–H(8*B*)–π 3.4360 Å).

For the complexes **I** and **II** there exist both the strong absorption bands at ~1530 and 1250 cm^{-1} can be assigned to the triazole ring stretching vibrations. The triazole out-of-plane ring absorption both can be observed at ~630 cm^{-1} [11] for the complexes **I** and **II**. These results are in agreement with the X-ray result.

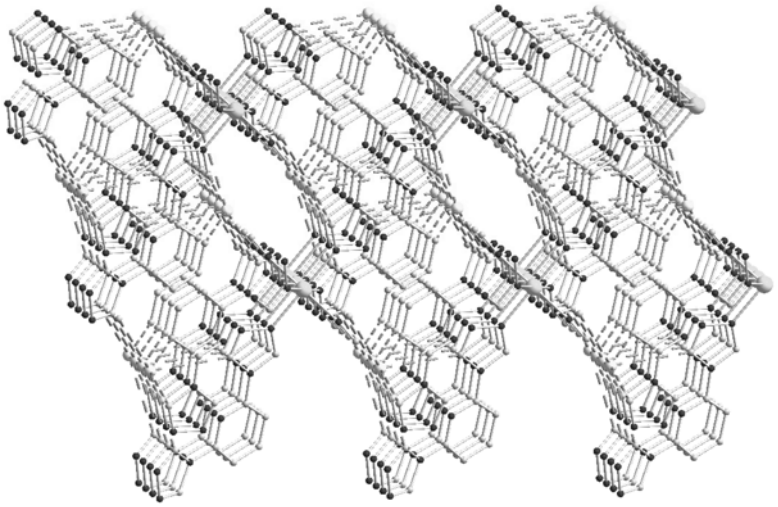


Fig. 2. The three-dimensional supra-molecular packing architecture of **I**.

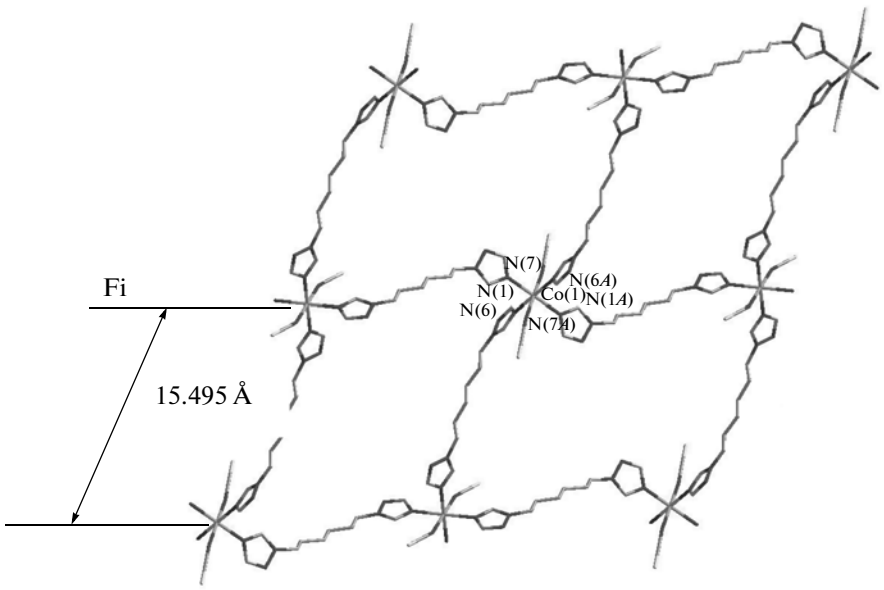


Fig. 3. Schematic representation of the (4,4) network topology of **II**.

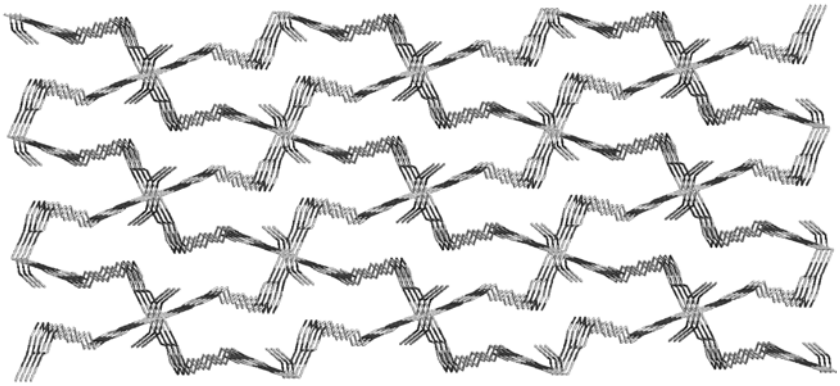


Fig. 4. View of the 1D channel in the 3D supra-molecular structure along the *x* axis in complex **II**.

As shown in Fig. 4, the 1D channel in the 3D supra-molecular structure along the *x* axis in complex **II** also reveals that there is still great potential in the construction of those novel coordination polymers with highly flexible bis-triazole ligands.

ACKNOWLEDGMENTS

This present work was supported financially by Tianjin Educational Committee (20120508).

REFERENCES

1. Hoskins, B.F., Robson, R., and Slizys, D.A., *J. Am. Chem. Soc.*, 1997, vol. 119, p. 2952.
2. Munakata, M., Wu, L.P., Sowa, T.K., et al., *Inorg. Chem.*, 1997, vol. 36, p. 5416.
3. Yaghi, O.M. and Groy, H., *J. Am. Chem. Soc.*, 1996, vol. 118, p. 9096.
4. Bino, A., Ardon, M., Lee, D., et al., *J. Am. Chem. Soc.,* 2002, vol. 124, p. 4578.
5. Barnett, S.A. and Champness, N.R., *Coord. Chem. Rev.*, 2003, vol. 246, p. 145.
6. Effendy, F., Marchetti, C., Pettinari, R., et al., *Inorg. Chem.*, 2004, vol. 43, p. 2157.
7. Yi, L., Yang, X., Lu, T.B., and Cheng P., *Cryst. Growth Des.*, 2005, vol. 3, p. 1215.
8. Torres, J., Lavandera, J.L., Cabildo, P., et al., *J. Heterocycl. Chem.*, 1988, vol. 25, p. 771.
9. Sheldrick, G.M., *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
10. Sheldrick, G.M., *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. Drabent, K., Bialonska, A., and Ciunik Z., *Inorg. Chem.*, 2004, vol. 7, p. 224.