



Synthesis, Crystal Structure and Fluorescent Properties of 1D New Double Chain Silver(I) Complex

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A novel silver(I) complex $[Ag(btzx)_2(NO_3)]_n$ [complex **1**, where btzx = *m*-xylylenebis(tetrazole)] is synthesized and characterized by elemental analysis, IR, powder and single crystal X-ray diffraction. The crystal structural analysis shows that silver center is four-coordinated in a distorted tetrahedral geometry by four nitrogen atoms from four different btzx and there are very weak interactions exist between Ag(I) and NO_3^- anions. This complex displays a 1D ladder-like double chain framework, which is further fabricated into a 2D supramolecular framework *via* π - π interactions. The fluorescence properties of complex **1** were investigated.

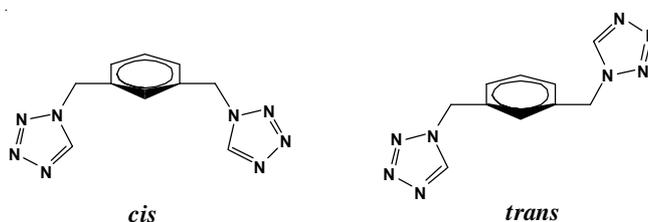
Keywords: *m*-Xylylenebis(tetrazole), Flexible ligand, Silver complex, Coordination polymers.

INTRODUCTION

In recent years, metal-organic frameworks (MOFs) have been rapidly developed and received great attention due to their fantastic structures such as cage, honeycomb and multidimensional framework¹⁻³ and their potential applications as functional materials in magnetism, ionic/molecular recognition, selective guest inclusion⁴⁻⁸. It is known that the construction of metal-organic frameworks mainly depends on the nature of organic bridging units and metal ions as well as the counter anions. Flexible ligands can adopt varied conformations and coordination modes according to the different geometric requirements of the metal ions and as a result may offer metal-organic frameworks with unique structures and useful properties^{9,10}. As it is known, ligands containing tetrazole groups are another class of N-heterocyclic building blocks, which are used extensively in crystal engineering^{11,12}. The tetrazole group has different coordination modes that could result in different solid-state architectures when reacting with metal ions compared to the pyridyl function.

To further investigate the nature of flexible ligands and their coordination polymers, *m*-xylylenebis(tetrazole) (btzx) were synthesized. Due to the presence of the methylene group and tetrazole, *m*-xylylenebis(tetrazole) (btzx) is an interesting flexible multidentate ligand (**Scheme-I**). The coordination chemistry of ligand btzx is less studied and there is only one FeII polymer reported by Gamez *et al.*¹³. Herein, we report the synthesis, crystal structure and fluorescent property of an

infinite 1D double chain silver(I) complex based on flexible btzx ligand.



Scheme-I: 'cis' and 'trans' conformations of flexible ligand btzx

EXPERIMENTAL

All chemicals were of reagent-grade quality, obtained from commercial sources and used as received without further purification. Ligand btzx was synthesized according to the literature¹³. Elemental analyses were determined using a Vario EL III elemental analyzer. The IR spectra were recorded in the 4000-400 cm^{-1} region using KBr pellets and a Nicolet AVATAR-370 spectrometer. Powder X-ray diffraction patterns were recorded on a Rigaku D/max-2550 X-ray diffractometer with graphite monochromatic $CuK\alpha$ (1.54056 Å) radiation at 40 kV/250 mA at room temperature.

Synthesis of complex 1: An aqueous solution (5 mL) of $AgNO_3$ (17.0 mg, 0.1 mmol) was added slowly to a solution of btzx (48.4 mg, 0.2 mmol) in methanol (10 mL) to give a clear solution. It was stirred for 10 min at room temperature. Colourless block crystals for X-ray diffraction were obtained

upon slow evaporation of the solvent after two weeks. Yield: 46 % based on Ag. Anal. Calcd for $C_{20}H_{20}N_{17}O_3Ag$ (654.4): C 36.71; H 3.08; N 36.39 %. Found: C 36.43; H 3.23; N 36.45 %. IR (KBr pellet, cm^{-1}): 3113m, 1485s, 1456m, 1435w, 1421s, 1375m, 1350s, 1253w, 1167s, 1109m, 1099s, 1024w, 978m, 893m, 823w, 736s, 717s, 661s, 599w, 573w.

X-Ray crystallography. Single crystal diffraction data for complexes **1** were collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Empirical absorption corrections were applied using SADABS program. The structures were determined by direct method with SHELXS-97 program and refined by full-matrix least squares on F^2 with SHELXL-97 program¹⁴. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically. Molecular graphics were drawn with XP and Diamond software. The crystal data and refinement results are given in Table-1. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 912459 and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT DETAILS FOR COMPLEX **1**

Empirical formula	$C_{20}H_{20}N_{17}O_3Ag$
Formula weight	654.4
Temperature (K)	293
Wavelength (\AA)	0.71073 A
Crystal colour	Colourless
Crystal size (mm)	$0.26 \times 0.06 \times 0.02$
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions: a, b, c (\AA)	9.729(6), 11.647(8), 12.779(8)
α, β, γ ($^\circ$)	115.838(7), 94.613(7), 100.906(7)
Volume (\AA^3)	1257.8(14)
Z	2
Calculate density (Mg/m^3)	1.728
Absorption coefficient (mm^{-1})	0.864
$F(000)$	660
θ range for data collection ($^\circ$)	1.98 to 27.17
Index ranges	$-11 \leq h \leq 12, -14 \leq k \leq 8, -15 \leq l \leq 16$
Reflections collected	7398
Independent [Rint]	5317
Completeness to $\theta = 25.02$	94.9 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5317 / 0 / 378
GOOF on F^2	1.001
Final R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0666, wR2 = 0.1512
R (all data) ^a	R1 = 0.1114, wR2 = 0.1758
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	0.941 and -0.785
^a $R_1 = \sum F_o - F_c / \sum F_o $, $wR_2 = [\sum w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$	

RESULTS AND DISCUSSION

The reaction of silver(I) nitrate with *m*-xylylenebis-(tetrazole) (btzx) is carried out in 1:2 molar ratio in the methanol/water system by slow volatilization of the solvent and complex **1** can be isolated. The results of elemental analysis

for complex **1** are highly consistent with the theoretical requirements of their compositions. The title compound herein is stable in air and at room temperature with little sign of decomposition within several hours upon exposure to light. In solution, the complex tends to undergo decomposition to form an oily black product. In the IR spectra of complex **1**, compared with the strong absorption band of the tetrazole ring at 1477, 1161 and 968 cm^{-1} in free btzx this signal is shifted to slightly higher amplitudes 1487, 1167, 978 cm^{-1} and strong sharp bands at 3113 cm^{-1} and 736 cm^{-1} further indicate the C–H stretching and bending frequencies of the tetrazole ring. The absorption band at 1487, 1373, 1041, 858 cm^{-1} corresponds to the bidentately coordinated NO_3^- anion, which is in good agreement with the observed crystal structures.

Description of the crystal structure. X-ray crystallographic analysis revealed that compound **1** crystallized in the triclinic form with space group $P\bar{1}$. The asymmetric unit of **1** contained one silver(I) ion sitting on an inversion center with two btzx and one nitrate anion. The coordination environment around the silver atom in complex **1** is exhibited in Fig. 1 and the selected bond lengths and angles are listed in Table-2. Each Ag(I) ion is coordinated to four nitrogen atoms (N1, N8, N9 and N15) from four different btzx ligands with Ag–N bond distances (2.328(5)–2.510(9) \AA) form an highly distorted tetrahedral geometry. Meanwhile, the *cis* angles around the central Ag(I) atom vary from $84.7(3)^\circ$ to $158.7(2)^\circ$, indicating a highly distortion. The N2 atom in tetrazole ring is found to be disordered (with occupancies 0.56 and 0.44) as shown in Fig. 1. There are very weak interactions exist between Ag(I) and NO_3^- anions, which the Ag–O distances (2.70 and 2.74 \AA) are shorter than the sum of van der Waals radii of silver and oxygen atoms (3.10 \AA)^{15,16}.

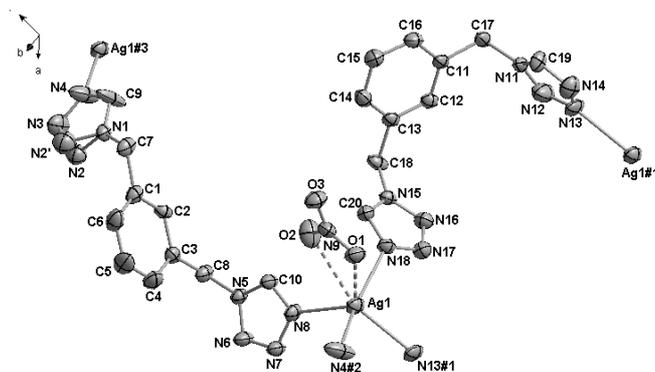


Fig. 1. Coordination environment around the Ag(I) center in complex **1** at 30 % probability, H atoms are omitted for clarity. Symmetry code: #1 $x, y, z-1$; #2 $-x+2, -y+1, -z+1$; #3 $x, y, z+1$; #4 $x+1, y-1, z$

TABLE-2
SELECTED BOND LENGTHS (\AA) AND
BOND ANGLES ($^\circ$) FOR COMPLEX **1**

Bond	d	Bond	d
Ag(1)-N(8)	2.328(5)	Ag(1)-N(18)	2.501(6)
Ag(1)-N(13)#1	2.346(6)	Ag(1)-N(4) #2	2.510(9)
Angle	ω	Angle	ω
N(8)-Ag(1)-N(13)#1	120.3(2)	N(13)#1-Ag(1)-N(18)	95.4(2)
N(8)-Ag(1)-N(18)	94.56(2)	N(13)#1-Ag(1)-N(4)#2	84.7(3)
N(8)-Ag(1)-N(4) #2	103.9(2)	N(18)-Ag(1)-N(4) #2	158.7(2)
Symmetry code: #1 $1-x, -y, 1-z$; #2 $x, y, -1+z$; #3 $x, y, 1+z$			

In complex **1** the ligand exhibits *trans* and *cis* configuration (**Scheme-1**) for the asymmetrical btzx, respectively. In complex **1**, the dihedral angle between the two terminal tetrazole groups with respect to the average plane of the phenyl ring in the asymmetric *cis*-configured btzx ligand is 64.0° and 71.5°, whereas in the *trans*-configured btzx ligand, the dihedral angle between the phenyl and tetrazole rings is 88.7° and 88.0°. Two *cis*-btzx ligands link adjacent two silver atoms to form a 24-membered $[\text{Ag}_2(\text{btzx})_2]$ metallacyclic ring, which is further connected through *trans*-configured btzx ligands to form a double chain ladder (Fig. 2). The Ag...Ag distance linked by *cis*-btzx is 10.33 Å in $[\text{Ag}_2(\text{btzx})_2]$ metallacyclic rings, whereas the Ag...Ag distance linked by *trans*-btzx is 12.78 Å. Furthermore, the centroid-centroid distances between paralleled tetrazole rings of two btzx ligands in neighboring 1D chain are 3.58 Å and 3.71 Å, respectively (Fig. 3). The molecule of complex **1** is stabilized by the π - π interactions into a 2D supramolecular framework.

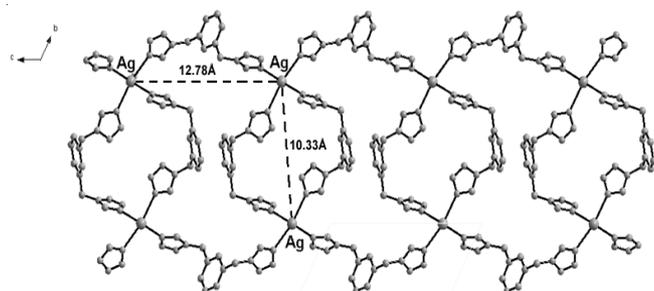


Fig. 2. Double-strand 1D ladder with 24-membered macrometallacyclic rings viewed from a axis, H₂O and NO₃⁻ are omitted for clarity

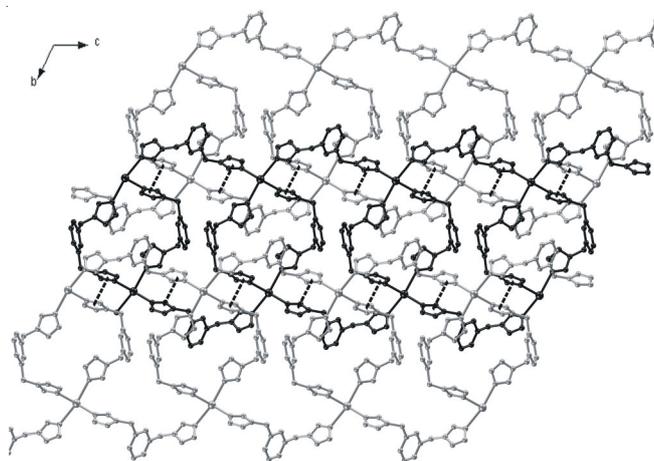


Fig. 3. Crystal packing from a axis. Interchain π - π interactions are highlighted by black dashes

Fluorescence: The pure phase of the products was confirmed by X-ray powder diffraction patterns (Fig. 4). The fluorescence properties of free btzx ligand and its Ag(I) complex **1** were investigated in the solid state at room temperature (Fig. 5). The maxima of emission band is observed at 360 nm ($\lambda_{\text{ex}} = 308$ nm) for free btzx ligand. For complex **1**, the fluorescence shows the blue-shift of wavelength and the obviously increasing of fluorescence compared to that of free btzx, which can be assigned to metal-to-ligand charge-transfer and the stacking of crystal structure^{13,17}.

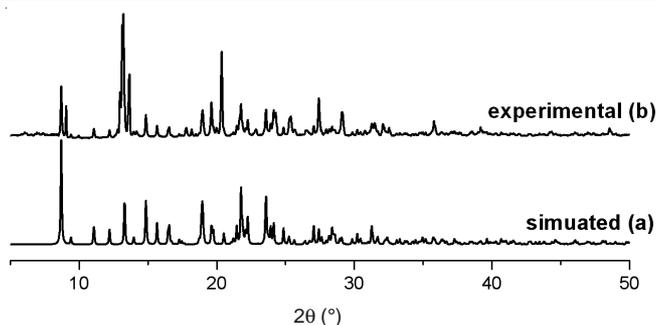


Fig. 4. X-ray powder diffraction patterns of simulated (a) and as prepared complex (b)

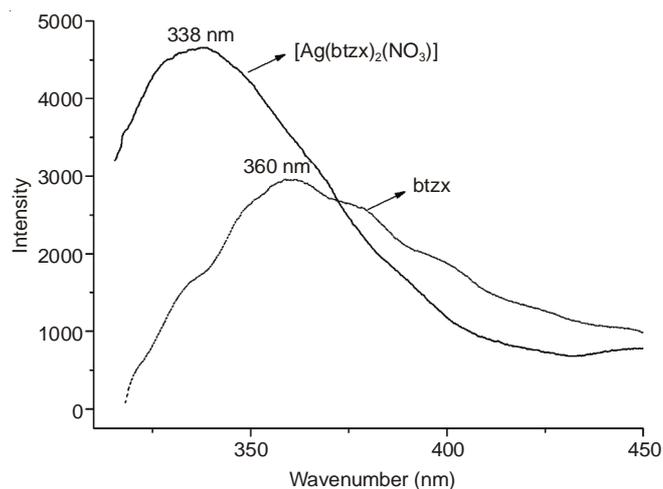


Fig. 5. Solid-state emission spectra of compound **1** and the free ligand btzx recorded at room temperature ($\lambda_{\text{ex}} = 308$ nm)

Conclusion

Novel 1D double chain coordination polymer **1** was synthesized by the solvent-volatile method and structurally determined by the single crystal X-ray diffraction analysis. The element and IR analyses were in good agreement with the theoretical requirements of their compositions.

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REFERENCES

1. B. Nepal and S. Das, *Angew. Chem. Int. Ed. Engl.*, **52**, 7224 (2013).
2. H. Li, W. Shi, K. Zhao, Z. Niu, H. Li and P. Cheng, *Chem. Eur. J.*, **19**, 3358 (2013).
3. I.H. Park, R. Medishetty, S.S. Lee and J.J. Vittal, *Chem. Commun.*, **50**, 6585 (2014).
4. G.A. Senchyk, A.B. Lysenko, A.A. Babaryk, E.B. Rusanov, H. Krautscheid, P. Neves, A.A. Valente, I.S. Goncalves, K.W. Kramer, S.X. Liu, S. Decurtins and K.V. Domasevitch, *Inorg. Chem.*, **53**, 10112 (2014).
5. J. Cui, N. Gao, C. Wang, W. Zhu, J. Li, H. Wang, P. Seidel, B.J. Ravoo and G. Li, *Nanoscale*, **6**, 11995 (2014).
6. D. Liu, X. Liu, Y. Liu, Y. Yu, F. Chen and C. Wang, *Dalton Trans.*, **43**, 15237 (2014).
7. A. Sachse, R. Ameloot, B. Coq, F. Fajula, B. Coasne, D. De Vos and A. Galarneau, *Chem. Commun.*, **48**, 4749 (2012).

8. Z. Guo, T. Kobayashi, L.L. Wang, T.W. Goh, C. Xiao, M.A. Caporini, M. Rosay, D.D. Johnson, M. Pruski and W. Huang, *Chem. Eur. J.*, **20**, 16308 (2014); 10.1002/chem.201403884.
9. T. Ni, F. Xing, M. Shao, Y. Zhao, S. Zhu and M. Li, *Cryst. Growth Des.*, **11**, 2999 (2011).
10. F. Evangelisti, R. Guttlinger, R. More, S. Lubner and G.R. Patzke, *J. Am. Chem. Soc.*, **135**, 18734 (2013).
11. M. Joas, T.M. Klapotke, J. Stierstorfer and N. Szimhardt, *Chem. Eur. J.*, **19**, 9995 (2013).
12. M.-X. Li, H. Wang, S.-W. Liang, M. Shao, X. He, Z.-X. Wang and S.-R. Zhu, *Cryst. Growth Des.*, **9**, 4626 (2009).
13. M. Quesada, F. Prins, E. Bill, H. Kooijman, P. Gamez, O. Roubeau, A.L. Spek, J.G. Haasnoot and J. Reedijk, *Chem. Eur. J.*, **14**, 8486 (2008).
14. G.M. Sheldrick, SHELXL97, A Program for the Refinement of Crystal Structures from X-Ray Data, University of Göttingen, Göttingen, Germany (1997).
15. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
16. S.-S. Sun, J.A. Anspach and A.J. Lees, *Inorg. Chim. Acta*, **351**, 363 (2003).
17. Z.Y. Zhang, Z.P. Deng, L.H. Huo, H. Zhao and S. Gao, *Inorg. Chem.*, **52**, 5914 (2013).