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Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 875 (2008) 339-345

www.elsevier.com/locate/molstruc

Solvothermal syntheses, crystal structures, and luminescent properties of two novel silver(I) coordination polymers containing 5-aryl-substituted tetrazolate ligands

Yang Chen^a, Zhi-Gang Ren^a, Hong-Xi Li^a, Xiao-Yan Tang^a, Wen-Hua Zhang^a, Yong Zhang^a, Jian-Ping Lang^{a,b,*}

^a School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, People's Republic of China ^b State Key Laboratory of Coordination Chemistry, Nanjiang University, Nanjing 210093, Jiangsu, People's Republic of China

> Received 3 March 2007; received in revised form 4 May 2007; accepted 8 May 2007 Available online 13 May 2007

Abstract

The solvothermal reactions of AgNO₃, NaN₃, with benzonitrile or 4-cyanopyridine in methanol/water yield two novel metal–organic coordination polymers, $[Ag(\mu_3-phtta)]_n$ (1) (phtta = 5-phenyltetrazolate) and $\{Ag[\mu_4-(4-pytta)]\}_n$ (2) [4-pytta = 5-(4-pyridyl)tetrazolate], respectively. The two reactions were involved in the *in situ* formation of 5-aryl-substituted tetrazolate ligands (phtta and pytta) through [2 + 3] cycloaddition reactions of azide anion with benzonitrile or 4-cyanopyridine. Compounds 1 and 2 were characterized by elemental analysis, IR spectra, and single-crystal X-ray crystallography. Compound 1 has a one-dimensional double-chain structure in which centrosymmetric dimeric [Ag(phtta)]₂ units are interconnected by four Ag–N bonds. These double-chains are further stacked into a 2D layer network through $\pi-\pi$ interactions between tetrazolyl rings and interactions between Ag⁺ and phenyl group or tetrazolyl ring. Compound 2 has an intriguing 3D non-interpenetrated supramolecular structure in which a 2D layer network with $(4.8^2)_{Ag}(4.8^2)_{pytta}$ topology holds the adjacent layers together via interactions of Ag⁺ ions in one layer with 4-N atoms of pytta ligands in the other. Photoluminescence studies revealed that solids 1 and 2 exhibit strong blue fluorescent emissions at $\lambda_{max} = 422$ and 390 nm ($\lambda_{ex} = 345$ nm), respectively, at ambient temperature.

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Keywords: Silver(I); Coordination polymer; Tetrazolate ligands; Solvothermal synthesis; Crystal structures; Luminescence properties

1. Introduction

The construction of supramolecular complexes from silver(I) salts and multi-topic N-containing ligands has recently attracted much attention due to their intriguing topology structures [1–8], and their potential applications in fluorescence [9–13], electrochemical properties [14–16], electrical conductivity [17], materials science [18], and antimicrobial properties [19]. These compounds are mainly prepared from routine solution reactions [1–6,10–20] or

hydro(solvo)thermal reactions of silver(I) salts with organic components [7–9,21–35]. In later reactions, various N-containing ligands were found to be generated *in situ* from inorganic and/or organic components under the presence of metal ions. For example, some tetrazolate ligands could be prepared *in situ* through so-called Demko-Sharpless [2 + 3] cycloaddition reactions of organic nitriles with azide anion in the presence of metal ions such as Zn^{2+} , Cd^{2+} , Ag^+ , and Cu^+ [22–35]. In the case of silver/tetrazolate complexes, only six examples have been reported up to now and they were all prepared from this unique cycloaddition reaction. The tetrazolate ligands in these structures are mainly 5-alkyl-substituted tetrazolates [7,8] and only one is 5-aryl-substituted tetrazolate [8]. Being aware of the fact that the chemistry of silver complexes with

^{*} Corresponding author. Address: School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, People's Republic of China. Tel.: +86 512 6588 2865; fax: +86 512 6588 0089.

E-mail address: jplang@suda.edu.cn (J.-P. Lang).

^{0022-2860/\$ -} see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2007.05.007

5-aryl-substituted tetrazolates are less unexplored, we chose benzonitrile and 4-cyanopyridine and carried out their reactions with sodium azide at solvothermal conditions and two $[Ag(\mu_3-phtta)]_n$ (1) (phtta = 5-phenyltetrazolate) and $\{Ag[\mu_4-(4-pytta)]\}_n$ (2) [4-pytta = 5-(4-pyridyl)tetrazolate] were isolated therefrom. Herein, we report their syntheses, crystal structures, and luminescent properties.

2. Results and discussion

2.1. Preparation and characterization of 1 and 2

The reaction of AgNO₃ with equimolar sodium azide and 2.5 equiv. of benzonitrile in H₂O/MeOH (v/ v = 1:2.5) under solvothermal conditions at 150 °C for 67 h gave rise to 1 as brown plates in 68.3% yield. On the other hand, analogous reactions of 1:1:2.5 AgNO₃/NaN₃/ 4-cyanopyridine at similar conditions produced colorless prismatic crystals of 2 in a relatively low yield (24.2%). Formation of 1 and 2 was confirmed by their elemental analyses and IR spectra. The absence of the cyano group in the range of 2200 cm^{-1} and the appearance of a new stretching vibration of tetrazolate anion at ca. 1400 cm^{-1} in the IR spectrum are line with the in situ formation of tetrazolate ligand generated by a [2+3] cycloaddition reaction of benzonitrile or 4-cvanopyridine with azide anion [24,30,31]. Short reaction time (<10 h) or low reaction temperature (<100 °C) or low molar ratio of reagents (e.g. AgNO₃/ NaN_3 /benzonitrile (or 4-cyanopyridine) = 1:1:1) for these reactions always resulted in a mixture of a small amount of 1 or 2 coupled with a large amount of unreacted starting materials. The IR spectrum of the mixture revealed the presence of the strong stretching vibrations of azide group (2050 cm^{-1}) and cyano groups (2200 cm^{-1}) of benzonitrile or 4-cyanopyridine. In addition, prolonged reaction time (>100 h) and high reaction temperature (>180 °C) for these reactions afforded 1 in a very low yield (<1%). The reason for this may be due to the trimerization of benzonitrile or

4-cyanopyridine into 1,3,5-triazine derivatives at reaction conditions [36–38]. Solids 1 and 2 are stable towards air and moisture and insoluble in common organic solvents such as DMF·DMSO, MeCN, toluene, MeOH, and CH₂Cl₂. The elemental analyses of 1 and 2 are consistent with their chemical formula. The identities of 1 and 2 were finally confirmed by X-ray crystallography.

2.2. Molecular structure of 1

Compound 1 crystallizes in the monoclinic space group $P2_1/n$ and the asymmetric unit consists of an Ag⁺ ion and a phtta anion. Compound 1 has a one-dimensional doublechain structure (extending along the c axis) in which two parallel $[Ag(phtta)]_n$ chains are alternatively arranged so that the Ag1 atom in one chain further interacts with the N2 of the phtta ligand of the other chain (Fig. 1). Alternatively, the 1D double-chain structure of 1 may be viewed as being built of centrosymmetric dimeric [Ag(phtta)]₂ units linked by four Ag-N bonds (e.g. Ag1-N3B, Ag1A-N3C, Ag1C-N3A, Ag1E-N3). In the structure of 1, each phtta ligand coordinates to three Ag^+ ions and serves as a μ_3 -1,2,3-tetrazolyl coordination mode, which was previously observed only in $[Zn(mtta)_2]_3(H_2O)$ (mtta = 5-methyltetrazolate) [29]. The Ag1 center is coordinated by N1, N2A, and N3B, forming an approximate trigonal coordination geometry (Table 1). The Ag1...Ag1A separation within the dimeric unit is 3.689(6) Å while the Ag1E···Ag1A and Ag1···Ag1C contacts between the dimeric units are 4.009(6) Å. The former value is close to the sum of the van der Walls radii of two Ag atoms, suggesting weak Ag···Ag interactions. The mean Ag-N bond length of 2.272(4) Å is slightly longer than those containing trigonally-coordinated Ag such as $[Ag(mtta)]_n$ (2.238(6) Å [7] and 2.219(12) A [8]). It is interesting to note that in the crystal of 1, each 1D double-chain further binds to adjacent chains through π - π interactions between tetrazolyl rings and interactions between Ag⁺ and phenyl group or tetrazolyl ring to form a 2D layer structure (Fig. 2). The



Fig. 1. Perspective view of a section of the double-chain structure (extending along the *cs* axis) of 1 with labeling scheme and 50% thermal ellipsoid. Symmetry codes: A: -x + 2, -y, -z + 2; B: *x*, *y*, z + 1; C: -x + 2, -y, -z + 1; E: *x*, *y*, z - 1.

Table 1 Selected bond lengths (Å) and angles (°) for $[Ag(u_2-phtta)]_{1}$ (1)

believed bond lengths (γ) and angles (γ) for $[\gamma g(\mu_3 phtm)]_{\mu}$ (1)					
Ag(1)–N(1)	2.263(4)	Ag(1)–N(3B)	2.248(5)		
Ag(1)–N(2A)	2.304(5)	N(1)-N(2)	1.345(6)		
N(2)–N(3)	1.311(6)	N(3)–N(4)	1.351(7)		
C(1)–N(4)	1.341(7)	C(1)–N(1)	1.342(7)		
N(1)-Ag(1)-N(3B)	133.95(17)	N(2A)-Ag(1)-N(3B)	107.29(16)		
N(1)-Ag(1)-N(2A)	117.67(16)	N(1)-N(2)-Ag(1A)	125.2(3)		
N(2)–N(1)–Ag(1)	115.7(3)	N(3)-N(2)-Ag(1A)	125.4(4)		
N(2)–N(3)–Ag(1E)	127.2(4)	N(4)-N(3)-Ag(1E)	122.6(3)		
C(1)–N(1)–Ag(1)	137.4(4)	N(2)-N(3)-N(4)	109.9(4)		
N(4)-C(1)-N(1)	111.6(5)	C(1)-N(1)-N(2)	104.8(4)		
N(3)-N(2)-N(1)	109.4(4)	C(1)-N(4)-N(3)	104.2(4)		

shortest centroid–centroid distance between tetrazolyl rings is 3.380(7) Å, while that between Ag⁺ ion and phenyl group or tetrazolyl ring is 3.502(8) Å or 3.682(8) Å. The phenyl group and the tetrazolyl ring of the phtta ligand in 1 are not co-planar with their dihedral angle of 11°, which is probably due to those weak interactions.

2.3. Molecular structure of 2

Compound 2 crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit contains an Ag⁺ ion and a pytta anion. As shown in Fig. 3, the Ag1 atom is bound to one N5C from one pyridyl group and three N atoms (N1, N2A, N4B) from three tetrazolyl groups of four different pytta ligands, forming a rare trigonal pyramidal one. It

is noted that the Ag1–N4B distance (2.530(2) Å) is longer than the other three (2.253(2)-2.352(2) Å). As a whole, each pytta in 2 serves as a tetradentate ligand. In the structure of 2, the 1-N, 2-N, and 4-N atoms of the tetrazolate of each pytta ligand bind to three Ag⁺ ions, respectively, forming a μ_3 -1,2,4-tetrazolyl coordination mode that was observed in $[Ag(mtta)]_n$ [7,8]. If the longer Ag1–N4 bond is neglected, the structure shows a 2D three-connected (4,8) layer with a Schafli symbol $(4.8^2)_{Ag}(4.8^2)_{pytta}$ in which Ag1 and the tetrazolate work as 3-connecting nodes (Fig. 4). Interestingly, the resulting wavy 2D layer further holds the adjacent layers together via interactions of Ag⁺ ions in one layer with 4-N atoms of pytta ligands in the other, forming a unique 3D non-interpenetrated supramolecular structure (Fig. 5). The $Ag \cdot Ag$ contacts within the layer are 4.1137(11) Å while those between the layers are 6.2754(10) Å. Both contacts are too long to include any metal-metal interaction. Like the phtta ligand in 1, the pyridyl group of the pytta in 2 is also not co-planar with its tetrazolate ring, and the dihedral angel between them is 37.09(6)°.

2.4. Luminescent properties

It is well known that complexes containing silver(I) ions and nitrogen-containing ligands have been investigated for luminescence properties [9-13,39,40]. As shown in Fig. 6, compounds 1 and 2 showed strong luminescent properties



Fig. 2. Cell packing diagram of 1 looking along the *c* axis. The dashed lines represent the π - π interactions between tetrazolyl rings and those between Ag⁺ and phenyl group or tetrazolyl ring.



Fig. 3. Perspective view of the coordination environment around the silver(I) center of 2 with labeling scheme and 50% thermal ellipsoid. All hydrogen atoms are omitted for charity. Symmetry codes: A: -x + 2, -y + 1, -z; B: x, -y + 3/2, z + 1/2; C: -x + 1, y - 1/2, -z + 1/2; D: -x + 2, y - 1/2, -z - 1/2; E: x + 1, -y + 3/2, z - 1/2.

in the solid state at ambient temperature. When excited at $\lambda_{ex} = 345$ nm, the luminescent spectra of 1 and 2 exhibited maximal emission peaks at 422 nm (1) and 390 nm (2), respectively. The possible origin of these peaks is tentatively attributed to ligand-to-ligand transitions from the phtta ligands in 1 or the pytta ligands in 2, which are in agreement with silver(I) coordination polymers of N-containing multi-topic ligands reported by others [13,40]. In addition, the relatively efficient $\pi - \pi$ interactions between tetrazolyl rings in 1 may account for the red shift of the emission peak in the spectrum of 1 relative to that of 2.

3. Conclusions

In this paper, we demonstrated the successful syntheses of two new silver(I) coordination polymers (1 and 2) containing phtta and pytta ligands from reactions of AgNO₃, NaN₃ and benzonitrile or 4-cyanopyridine at solvothermal conditions. The two reactions are involved in the *in situ* generation of two new tetrazolate ligands (phtta and pytta) from the [2 + 3] cycloaddition reaction of organonitriles and azide anion. X-ray analysis revealed that 1 contains a 1D double-chain structure and each chain in the crystal



Fig. 4. The 2D network in 2 extending along the bc plane. All the Ag1-N4 bonds and the hydrogen atoms are omitted for clarity.



Fig. 5. Cell packing diagram of 2 looking along the *a* axis.



Fig. 6. Emission spectra of **1** (dashed line) and **2** (solid line) in the solid state at ambient temperature ($\lambda_{ex} = 345$ nm).

further stacks with its neighboring chains into a 2D network through the π - π interactions between tetrazolyl rings and between Ag⁺ and phenyl group or tetrazolyl ring. Compound 2 has an intriguing 3D non-interpenetrated supramolecular structure in which a 2D layer with a $(4.8^2)_{Ag}(4.8^2)_{pytta}$ topology combines with its adjacent layers via interactions of Ag⁺ ions in one layer with the 4-N atoms of the pytta ligands in the other. The tetrazolate ligands in 1 and 2 show μ_3 -1,2,3-tetrazolyl and μ_3 -1,2,4-tetrazolyl mode, respectively and the Ag(I) center in the structure of 2 adopts a rare trigonal pyramidal coordination geometry. In addition, solids 1 and 2 were demonstrated

to display strong blue fluorescence emissions at room temperature, which suggested that they might be good bluelight-emitted materials. The successful isolation of 1 and 2 suggests that more interesting silver(I) coordination polymers of tetrazolate derivatives can be prepared through [2 + 3] cycloaddition reactions of other aryl-nitriles with azide at solvothermal conditions. Studies in this respect are under way in our laboratory.

4. Experimental

4.1. General

All the chemicals were obtained from commercial sources and used as received. The IR spectra were recorded on a Varian 1000 FT-IR (Scimitar Series) spectrometer as KBr disks ($4000-400 \text{ cm}^{-1}$). The elemental analyses for C, H, and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. All manipulations were carried out in air. Emission and Excitation spectra were performed on a Perkin-Elmer LS55 spectrofluorometer with a red-sensitive R928 photomultiplier.

4.2. Synthesis

Caution. Metal azides may be explosive. At all times, great care must be taken when handling these materials.

4.2.1. Preparation of 1

A mixture of AgNO₃ (0.1699 g, 1.0 mmol), NaN₃ (0.065 g, 1.0 mmol), benzonitrile (0.2578 g, 2.5 mmol),

water (2.0 ml) and methanol (5 ml) was stirred for five minutes in air and then transferred into a 15 ml Teflon-lined reactor and then sealed. The reactor was heated in an oven to 150 °C for 67 h and then cooled to room temperature at a rate of 5 °C h⁻¹. The brown plate crystals were elutriated with methanol several times and dried in air. Yield: 0.1729 g (68.3%). Anal. Calcd. for C₇H₅AgN₄: C, 33.23; H, 1.99; N, 22.14. Found: C, 33.64; H, 1.97; N, 22.05%. IR (KBr disk, cm⁻¹): 3399 (w), 3064 (w), 3044 (w), 1443 (vs), 1364 (s), 1280 (m), 1138 (m), 1072 (m), 1010 (m), 927 (w), 789 (m), 726 (vs), 688 (vs), 504 (w), 458 (w).

4.2.2. Preparation of 2

Compound 2 was prepared as above starting from AgNO₃ (0.1699 g, 1.0 mmol), NaN₃ (0.065 g, 1.0 mmol), 4-cyanopyridine (0.2603 g, 2.5 mmol), water (2.0 ml) and methanol (5 ml). Yield: 0.0614 g (24.2%) of colorless prismatic crystals. Anal. Calcd for C₆H₄AgN₅: C, 28.37; H, 1.59; N 27.57. Found: C, 28.22; H, 1.58; N 27.61%. IR (KBr disk, cm⁻¹): 3384 (w), 3082 (w), 3031 (w), 1685 (w), 1618 (vs), 1554 (m), 1454 (s), 1418 (s), 1377 (s), 1320 (m), 1225 (s), 1138 (s), 1070 (w), 1005 (s), 843 (vs), 761 (s), 735 (m), 709 (vs), 550 (m), 450 (m).

4.3. X-ray crystallography

All measurements were performed on a Rigaku Mercury CCD X-ray diffractometer (3KV, sealed tube) at 153 K, using graphite monochromated Mo-K α ($\lambda = 0.71070$ Å). with А brown plate of 1 dimensions $0.03 \times 0.10 \times 0.25 \text{ mm}^3$ and a colorless prism of **2** with dimensions $0.17 \times 0.28 \times 0.40$ mm³ were mounted on glass fibers with grease. Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystal. Indexing was performed from 6 images, each of which was exposed for 4 s (for 1) and 2 s (for 2). A total of 720 oscillation images for each were collected in the range $6.09^{\circ} < 2\theta < 50.70^{\circ}$ for 1 and $6.10^{\circ} < 2\theta < 50.68^{\circ}$ for 2. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 1.3, 2001), and an absorption correction (multi-scan) was applied, which resulted in transmission factors ranging from 0.732 to 0.917 for 1 and 0.380 to 0.609 for 2. The reflection data were also corrected for Lorentz and polarization effects Table 2.

The crystal structures of 1 and 2 were solved by direct methods [41], and expanded using Fourier techniques [42]. All non-hydrogen atoms were refined anisotropically, and all other hydrogen atoms were placed in geometrically idealized positions (C–H = 0.97 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2 U_{\rm eq}({\rm C})$. All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku/MSC, Ver. 3.60, 2004). Important crystal data and collection sand refinement parameters for 1 and 2 are summarized in Table 3.

Selected bond lengths (Å) and bond angles (°) for $\{Ag[\mu_4-(4-pytta)]\}_n$ (2)					
Ag(1)–N(1)	2.253(2)	Ag(1)–N(5C)	2.288(2)		
Ag(1)–N(2A)	2.352(2)	Ag(1)-N(4B)	2.530(2)		
C(1)–N(1)	1.341(3)	C(1)–N(4)	1.342(3)		
N(1)–N(2)	1.353(3)	N(2)–N(3)	1.313(3)		
N(3)-N(4)	1.345(3)				
N(1)-Ag(1)-N(5C)	142.83(8)	N(1)-Ag(1)-N(2A)	105.80(8)		
N(5C)-Ag(1)-N(2A)	101.91(8)	N(1)-Ag(1)-N(4B)	88.20(8)		
N(5C)-Ag(1)-N(4B)	97.94(8)	N(2A)-Ag(1)-N(4B)	121.66(8)		
C(1)-N(1)-Ag(1)	130.11(18)	N(2)-N(1)-Ag(1)	123.28(16)		
N(3)-N(2)-Ag(1A)	121.18(17)	N(1)-N(2)-Ag(1A)	129.20(16)		
C(1B)–N(4B)–Ag(1)	125.85(17)	N(3B) - N(4B) - Ag(1)	111.47(16)		
C(5C)–N(5C)–Ag(1)	124.81(18)	C(4C)-N(5C)-Ag(1)	117.84(18)		
N(1)-C(1)-N(4)	111.2(2)	C(1)-N(1)-N(2)	104.7(2)		
N(3)-N(2)-N(1)	109.5(2)	N(2)-N(3)-N(4)	109.5(2)		
C(1)-N(4)-N(3)	105.1(2)	C(5)-N(5)-C(4)	116.7(2)		

Table 3

Crystallographic data for $[Ag(\mu_3-phtta)]_n$ (1) and $\{Ag[\mu_4-(4-pytta)]\}_n$ (2)

	1	2
Empirical formula	C7H5N4Ag	C ₆ H ₄ N ₅ Ag
Formula weight	253.02	254.01
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
<i>a</i> (Å)	6.1015(12)	7.2691(15)
b (Å)	20.065(4)	11.092(2)
c (Å)	6.2962(13)	8.4619(17)
β (°)	108.14(3)	98.54(3)
$V(\text{\AA}^3)$	732.5(3)	674.7(2)
Ζ	4	4
$T(\mathbf{K})$	153	153
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.294	2.501
F (000)	488	488
μ (Mo-K α , cm ⁻¹)	2.688	2.922
Total no. of reflections	7081	6244
No. of unique reflections	1344	1234
No. of observed reflections $[I \ge 2.00\sigma (I)]$	1175	1178
No. of variables	109	109
R ^a	0.0419	0.0199
$wR^{\rm b}$	0.0869	0.0472
GOF ^c	1.045	1.149
Largest residual peaks and holes $(e/Å^3)$	1.311, -0.620	0.73, -0.523

Where n = number of reflections and p = total numbers of parameters refined.

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|.$ ^b $wR = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}.$ ^c $GOF = \{\sum [w((F_o^2 - F_c^2)^2) / (n-p)\}^{1/2}.$

Acknowledgements

This work was financially supported by the NNSF (No. 20525101), the NSF of Jiangsu Province (No. BK2004205), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20050285004), and the State Key Laboratory of Coordination Chemistry of Nanjing University and the Qin-Lan Project of Jiangsu Province in China. The authors also thank Prof. Zhong-Ni Chen of FJIRSM for his assistance in the measurement of luminescent properties of the title compounds.

Appendix A. Supplementary data

Crystallographic data in CIF format can be obtained free of charge from Cambridge Crystallographic data Center (CCDC Nos. 632200 (1) and 632201 (2)), 12 Union Road, Cambridge CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.05.007.

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