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Ag(I)-Mediated In situ Dehydrogenative Coupling of 3-Amino-1,2,4-triazole into 3,3′-Azobis(1,2,4-triazole) in Cd(II) Coordination Polymers

Pei-Xiu Yin,[†] Jian-Kai Cheng,[†] Zhao-Ji Li,[†] Lei Zhang,[†] Ye-Yan Qin,[†] Jian Zhang,[†] and Yuan-Gen Yao*,[†]

[†] *The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,*
The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

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Ag(I)-mediated in situ generation of 3,3′-azobis(1,2,4-triazole) (AzTAZ) from 3-amino-1,2,4-triazole (AmTAZ) through dehydrogenative coupling has been realized during the crystallization process of two Cd(II) coordination polymers with novel topological architectures: a (3, 4, 5)-connected $(4\cdot6^2)_2(4\cdot6^7\cdot8^2)_2(6^5\cdot10)$ net for $[Cd_2(AmTAZ)_2(AzTAZ)]_n$ (**1**) and a 4-connected $(6^2\cdot8^4)(6^4\cdot8^2)(6^5\cdot8)_2$ net for $[Cd(AzTAZ)_2(H_2O)]_n$ (**2**), whereas AmTAZ retains its original form in a heterometallic complex, $[Ag_2Cd(AmTAZ)_4]_n$ (**3**).

Recently, much effort has been directed toward the crystal engineering of coordination polymers involving in situ formation of organic building blocks.[1] In this context, hydro(solvo)thermal in situ ligand synthesis has been rapidly developed, mostly provoked by the advantages stemming from a simple operating step, environmental friendliness, and easiness to grow suitable single crystals.[1] Another advantage for in situ synthesis is that it provides an intriguing pathway for the elucidation of reaction mechanism and the discovery of new organic reactions.[1] To date, many types of in situ ligand reactions have been documented.[2] Yet, the discovery of new hydro(solvo)thermal in situ ligand synthesis from easily accessible starting materials is still a significant challenge because of their unpredictable results. Thus, a great deal of work is required to extend the knowledge of the construction of functional coordination polymers involving in situ ligand synthesis. On the other hand, Ag(I)-catalyzed reactions have provided an important approach for a myriad of organic transformations that have recently been reviewed.[3] Most of these reactions utilize the Lewis acid character of Ag(I) cation toward O and N atoms. In this communication, we wish to report a new example of Ag(I)-mediated in situ formation of AzTAZ from AmTAZ under hydrothermal conditions.

Originally, AgCl was incorporated into the $Cd(NO_3)_2$/HAmTAZ system to gain some heterobimetallic compounds with intriguing structures and properties. The hydrothermal treatment of $Cd(NO_3)_2$ with HAmTAZ in mixed solvents $H_2O/NH_3\cdot H_2O$ in the presence of AgCl at 130 °C through altering the ratio of starting materials produced two homometallic complexes, $[Cd_2(AmTAZ)_2(AzTAZ)]_n$ (**1**) and $[Cd(AzTAZ)_2(H_2O)]_n$ (**2**), and a heterometallic complex, $[Ag_2Cd(AmTAZ)_4]_n$ (**3**) (Scheme 1).[4] Unexpectedly, during the syntheses of **1** and **2**, AmTAZ is in situ transformed into AzTAZ, which, to the best of our knowledge, is first observed. Unlike other AzTAZ-based compounds, in which AzTAZ was predesigned from

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*To whom correspondence should be addressed. E-mail: yyg@fjirsm.ac.cn.

(1) (a) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771. (b) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W. S.; Schroder, M. *Chem. Commun.* **1997**, 1675. (c) Yang, Q. F.; Cui, X. B.; Yu, J. H.; Lu, J.; Yu, X. Y.; Zhang, X.; Xu, J. Q.; Hou, Q.; Wang, T. G. *Crystengcomm* **2008**, *10*, 1531. (d) Cheng, L.; Zhang, W. X.; Ye, B. H.; Lin, J. B.; Chen, X. M. *Inorg. Chem.* **2007**, *46*, 1135. (e) Zhang, X. M. *Coord. Chem. Rev.* **2005**, *249*, 1201. (f) Chen, X. M.; Tong, M. L. *Acc. Chem. Res.* **2007**, *40*, 162. (g) Zhou, X. P.; Li, D.; Wu, T.; Zhang, X. J. *Dalton Trans.* **2006**, 2435.

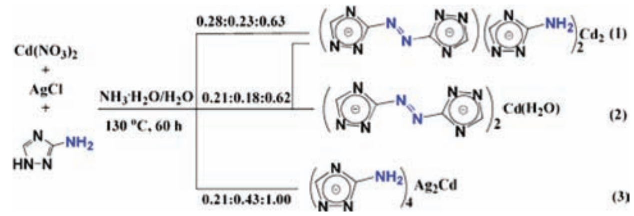
(2) (a) Hu, S.; Chen, J. C.; Tong, M. L.; Wang, B.; Yan, Y. X.; Batten, S. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5471. (b) Zhang, X. M.; Tong, M. L.; Gong, M. L.; Lee, H. K.; Luo, L.; Li, K. F.; Tong, Y. X.; Chen, X. M. *Chem.—Eur. J.* **2002**, *8*, 3187. (c) Liu, C. M.; Gao, S.; Kou, H. Z. *Chem. Commun.* **2001**, 1670. (d) Xiao, D. R.; Hou, Y.; Wang, E. B.; Lu, J.; Li, Y. G.; Xu, L.; Hu, C. W. *Inorg. Chem. Commun.* **2004**, *7*, 437. (e) Cheng, L.; Zhang, W. X.; Ye, B. H.; Lin, J. B.; Chen, X. M. *Inorg. Chem.* **2007**, *46*, 1135. (f) Xiong, R. G.; Xue, X.; Zhao, H.; You, X. Z.; Abrahams, B. F.; Xue, Z. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 3800. (g) Zheng, S. T.; Wang, M. H.; Yang, G. Y. *Inorg. Chem.* **2007**, *46*, 9503. (h) Li, X. J.; Cao, R.; Guo, Z. G.; Lu, J. *Chem. Commun.* **2006**, 1938.

(3) (a) Naodovic, M.; Yamamoto, H. *Chem. Rev.* **2008**, *108*, 3132. (b) Álvarez-Corral, M.; Muñoz-Dorado, M.; Rodirguez-Garcia, I. *Chem. Rev.* **2008**, *108*, 3174. (c) Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3199.

(4) Synthesis: for **1**, a mixture of HAmTAZ (0.053 g), $Cd(NO_3)_2\cdot4H_2O$ (0.087 g), AgCl (0.033 g), and mixed solvents H_2O (8.5 mL)/$NH_3\cdot H_2O$ (25%, 5 mL) was sealed in a Teflon-lined reaction vessel; for a mixture of **1** and **2**, a mixture of HAmTAZ (0.052 g), $Cd(NO_3)_2\cdot4H_2O$ (0.065 g), AgCl (0.026 g), and mixed solvents H_2O (8.5 mL)/$NH_3\cdot H_2O$ (25%, 5 mL); for **3**, a mixture of HAmTAZ (0.084 g), $Cd(NO_3)_2\cdot4H_2O$ (0.065 g), AgCl (0.062 g), and mixed solvents H_2O (8.5 mL)/$NH_3\cdot H_2O$ (25%, 5 mL) was sealed in a Teflon-lined reaction vessel. These vessels were heated at 130 °C for 60 h and then cooled to room temperature during 48 h. Red and yellow crystals of **1** (yield, 36% based on Cd) and **2** (yield, 12% based on Cd) and orange crystals of **3** (yield, 57% based on Cd) were isolated from yellow filtrate. Anal. Calcd for $C_4H_4CdN_8$ **1**: C, 17.37; H, 1.46; N, 40.52. Found: C, 17.21; H, 1.57; N, 39.92%. Anal. Calcd for $C_4H_4CdN_8O$ **2**: C, 16.42; H, 1.38; N, 38.30. Found: C, 16.28; H, 1.53; N; 37.63%. Anal. Calcd for $C_8H_{12}Ag_2CdN_{16}$ **3**: C, 14.55; H, 1.83; N, 33.93. Found: C, 14.43; H, 2.03; N, 33.35%.

(5) (a) Lee, K. Y. U.S. Patent 46 623 409A,**1986**.(b) Naud, D. L.; Hiskey, M. A.; Harry, H. H. *J. Energy Mater.* **2003**, *21*, 57. (c) Sivabalan, R.; Anniyappan, M.; Pawar, S. J.; Talawar, M. B.; Gore, G. M.; Venugopalan, S.; Gandhe, B. R. *J. Hazard. Mater.* **2006**, *137*, 672.

Scheme 1. Synthesis of Coordination Polymers **1**−**3**[a]



[a] The ratio for $Cd(NO_3)_2$/AgCl/HAmTAZ is shown with their corresponding mole used in the synthesis.

oxidation of AmTAZ with potassium permanganate,[5] the preparation of **1** and **2** provides a simple operating step for the construction of AzTAZ-based coordination polymers and makes the synthesis of AzTAZ comparatively more efficient. Compounds **1**−**3** are characterized by single-crystal X-ray diffraction.[6] Part of AmTAZ ligands retain their original form in **1**, whereas complete transformation occurs in **2**. This may be derived from the decrease in the amount of $Cd(NO_3)_2$ and AgCl, whereas an increase in the amount of HAmTAZ and AgCl for the synthesis of a mixture of **1** and **2** results in the formation of **3**. All these facts demonstrate that coordination polymers **1**−**3** are molar-ratio-dependent products.

Structural analysis of compound **1** reveals a three-dimensional framework. There is one Cd(II), one AmTAZ, and half a AzTAZ in the asymmetric unit of **1** (Figure 1a). The Cd(1) atom is ligated by one N atom from diazenen group and five triazole ring N atoms from two separate AzTAZ and three individual AmTAZ, showing an octahedron geometry. With Cd(1)−N(8) (2.743(3) Å) being much longer than other Cd−N bonds (2.290(3)−2.355(3) Å), the coordination polyhedron is severely distorted from the ideal octahedral. The AmTAZ ligand in commonplace μ_3-N1,N2,N3 bridging mode and AzTAZ in bis-bridging-chelating mode link Cd(II) centers to generate the 3D architecture of **1** (see Figure S1 in the Supporting Information). As described above, the resulting framework can be simplified as a (3,4,5)-connected $(4\cdot6^2)_2(4\cdot6^7\cdot8^2)_2(6^5\cdot10)$ net by reducing Cd(II) center to be a five-connecting node, AmTAZ to be a three-connecting node, and AzTAZ to be a four-connecting node, respectively (Figure 1b).

Different from that observed in **1**, AmTAZ is completely converted to AzTAZ in the case of **2**. Two crystallographically independent one-quarter occupied Cd(II) atoms, one-half-occupied AzTAZ ligand and half a water molecule are present in the asymmetric unit of **2** (Figure 1c). Cd(1) is surrounded by four symmetry-related N(3) atoms from four separate AzTAZ forming a perfect tetrahedral geometry. Cd(2), lying in the center of an elongated octahedron, is coordinated to four symmetry-related N(1) atoms in the basal plane and two water molecules at the apical positions. The shortest Cd(1)···N(4) separation of 2.942(2) Å indicates the absence of covalent bond between Cd(1) and the diazene group, Thus, AzTAZ adopts a bis-bridging mode, which is in sharp contrast with that found in **1**. The connectivity between Cd atoms and AzTAZ results in a 3D porous architecture, in which the coordinated water molecules as filling spacers occupy the 1D channel and form hydrogen bonds with the uncoordinated N(2) atom of triazole ring to further stabilize the framework (see Figure S2 in the Supporting Information). Thus, the overall network manifests an unreported 4-connected trinodal $(6^2\cdot8^4)(6^4\cdot8^2)(6^5\cdot8)_2$ topology for $(Cd1)(Cd2)(AzTAZ)_2$, which differs greatly from another two reported 4-connected trinodal nets.[7]

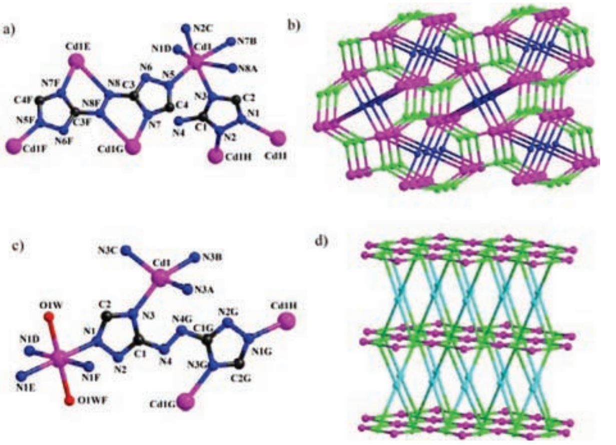


Figure 1. Perspective view of the coordination geometry of the Cd(II) centers and organic ligands in (a) **1** and (c) **2**. Topological representation of the 3D structures of (b) **1** and (d) **2**.

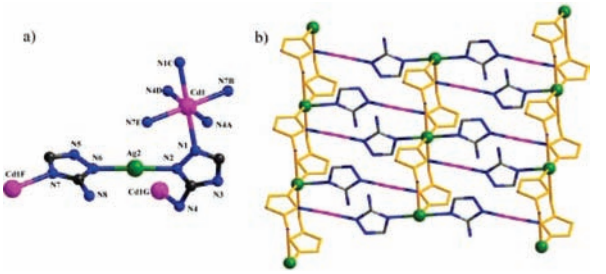


Figure 2. (a) Perspective view of the coordination geometry of Cd(II) and Ag(I) centers and AmTAZ. (b) 2D layered structure of **3**.

In the above two investigated complexes, the coplanar AzTAZ ligands lie across an inversion center at the midpoint of $N_{dia}-N_{dia}$ (Figure S3). Furthermore, the $N_{dia}-N_{dia}$ and $C-N_{dia}$ bond distances (1.262(5) and 1.399(4) Å for **1**, 1.272(3) and 1.405(2) Å for **2**) are comparatively similar. However, great difference in the coordination modes of AzTAZ (bis-bridging-chelating in **1** and bis-bridging in **2**) occurs. This may presumably be due to the additional incorporation of AmTAZ into the coordination sphere of Cd(II) in **1**, illustrating the existence of AmTAZ have important effect on the function of AzTAZ.

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(6) (a) Crystal data for **1**: $C_4H_4CdN_8$, M_r = 276.56, monoclinic, space group $P2_1/n$, a = 8.5883(11) Å, b = 8.8382(8) Å, c = 10.0357(11) Å, β = 91.114(12)°, V = 1179.66(2) Å^3, Z = 4, T = 293(2) K, D_c = 2.412 g cm^{-3}, R(int) = 0.0204, 5610 reflections collected, R_1 (wR_2) = 0.0221 (0.0687) and S = 1.009 for 1645 reflections with $I > 2\sigma(I)$. (b) Crystal data for **2**: $C_4H_4CdN_8O$, M_r = 292.55, orthorhombic, space group *Ibam*, a = 7.9911(7) Å, b = 10.1983(8) Å, c = 20.4588(18) Å, V = 1667.3(2) Å^3, Z = 8, T = 293(2) K, D_c = 2.331 g cm^{-3}, R(int) = 0.0124, 6029 reflections collected, R_1 (wR_2) = 0.0200 (0.0378) and S = 1.166 for 890 reflections with $I > 2\sigma(I)$. (c) Crystal data for **3**: $C_8H_{12}Ag_2CdN_{16}$, M_r = 660.48, triclinic, space group $P\bar{1}$, a = 6.6021(3) Å, b = 6.6711(5) Å, c = 9.6337(3) Å, α = 70.08(3)°, β = 71.84(2)°, γ = 87.15(3)°, V = 378.28(4) Å^3, Z = 1, T = 293(2) K, D_c = 2.899 g cm^{-3}, R(int) = 0.0231, 3023 reflections collected, R_1 (wR_2) = 0.0379 (0.0922) and S = 1.051 for 1480 reflections with $I > 2\sigma(I)$.

(7) (a) Lin, J. G.; Zang, S. Q.; Tian, Z. F.; Li, Y. Z.; Xu, Y. Y.; Zhu, H. Z.; Meng, Q. J. *Crystengcomm* **2007**, *9*, 915. (b) Qi, Y.; Che, Y. X.; Batten, S. R.; Zheng, J. M. *Crystengcomm* **2008**, *10*, 1027.

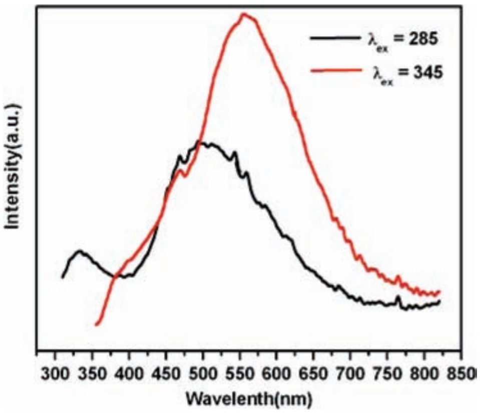

Figure 3. Fluorescence emission spectra of **3** with excitation of 285 and 345 nm, respectively.

An increase in the amount of HAmTAZ and AgCl for the synthesis of a mixture of **1** and **2** resulted in the formation of a heterometallic Ag/Cd complex, $[Ag_2Cd(AmTAZ)_4]_n$ (**3**), in which AmTAZ well-retains its original form. In the structure of **3**, the asymmetric unit possesses half a Cd(II), one Ag(I), and two AmTAZ (Figure 3a). Cd(1) has a six-coordinate octahedral geometry with six N atoms from six different AmTAZ, whereas Ag(2) is only linearly coordinated. AmTAZ presents two coordination modes, μ_3-N1,N2,N4 bridging mode (mode I) and μ_2-N1,N3 bridging mode (mode II) in this instance. Although μ_3-N1,N2,N3 bridging mode of AmTAZ has been well-known, μ_3-N1,N2,N4 bridging mode, to the best of our knowledge, has never been documented.[8] The Cd(II) centers are bridged by AmTAZ in mode I into a 1D double chain (Figure 2b, see Figure S4 in the Supporting Information), whereas AmTAZ in mode II coordinate to Ag(I) centers forming metalloligands, which connect the adjacent 1D double chains into the 2D neutral layer of **3** (Figure 2b).

Because of the relatively intricate conditions, the detailed investigation of the hydrothermal reaction mechanism presents a considerable challenge. In order to evaluate whether Ag(I) salts play crucial roles in the reaction process, compound **1** was chosen to carry out a detailed study: (i) in the presence of AgCl, various Cd(II) sources with different counterions, such as OAc^-, Cl^-, and Br^-, were used under identical conditions, compound **1** was also obtained, indicating that the anions of Cd(II) salts do not play significant roles in the formation of AzTAZ; (ii) without AgCl, the reactions through only altering Cd(II) sources (such as $Cd(OAc)_2$, $CdCl_2$ and $CdBr_2$) do not lead to compound **1** but to some white or pale-yellow powder. This fact shows that Ag(I) salt may act as the catalyst in the formation of AzTAZ; (iii) when Ag_2O or $AgNO_3$ were used instead of AgCl, compound **1** was also prepared; (iv) when various Ag(I) sources, such as Ag_2O and $AgNO_3$, were used alone under similar conditions, AmTAZ can also be converted into AzTAZ (see synthesis of AzTAZ in the Supporting Information). The latter two points further confirm the proposed speculation.

TGA-DTA was performed on crystalline samples from 35 to 900 °C under a nitrogen atmosphere. The frameworks are stable up to 425 °C for **1** and 320 °C for **3**, respectively. Beyond these temperatures the organic components begin to decompose and the frameworks are thus collapsed (see Figure S5 in the Supporting Information). Compound **3** displays interesting fluorescent phenomena with two strong fluorescent bands at λ_{max} = 510, 550 nm (λ_{ex} = 285, 345 nm) (Figures 3 and Figure S6 in the Supporting Information). As observed in $[Ag(TZ)]_\infty$,[9] these emission bands may be assigned to ^{1}[MLCT] excited state.

In conclusion, an Ag(I)-mediated in situ transformation from 3-amino-1,2,4-triazole to 3,3′-azobis(1,2,4-triazole) has been reported for the first time that accompanies metal−ligand coordination, affording two Cd(II) coordination polymers with novel topological architectures. On the other hand, 3-amino-1,2,4-triazole is kept intact in a heterobimetallic Ag/Cd complex. The syntheses of polymers in this work illustrate again that molar ratio of raw materials play important roles in realizing the diversity of coordination polymers. In view of the high nitrogen content of the ligands in this work, the potential uses as N-rich high-energy materials of these polymers will be investigated in the future.

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Supporting Information Available: X-ray crystallographic files in CIF format; synthesis of AzTAZ, the conformation and main geometric parameters for AzTAZ observed in **1** and **2**, 3D architectures of **1**−**2**, 1D double chain of Cd-AmTAZ in **3**, TG-DTA curves of **1** and **3**, and IR spectra of **1**−**3** and AzTAZ (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] (a) Su, C. Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 3576. (b) Patel, R.; Weller, M. T.; Price, D. J. *Dalton Trans.* **2007**, 4034. (c) Li, W.; Jia, H. P.; Ju, Z. F.; Zhang, J. *Cryst. Growth Des.* **2006**, *6*, 2136.

[9] Zhang, J. P.; Lin, Y. Y.; Huang, X. C.; Chen, X. M. *J. Am. Chem. Soc.* **2005**, *127*, 5495.