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Capturing a Metastable Silver(I) Compound of Pyrazine-2,3-dicarboxylic Acid

Di Sun, Geng-Geng Luo, Na Zhang, Zhan-Hua Wei, Cheng-Feng Yang, Rong-Bin Huang,* and Lan-Sun Zheng
State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry,
College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

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A metastable 3D supramolecular compound $[Ag(NH_3)_2]$-$[Ag_3(pzdca)_2(NH_3)_4]$ (H_2pzdca = pyrazine-2,3-dicarboxylic acid) (**1**) has been synthesized and characterized crystallographically. This study offers important information to in-depth understanding of the self-assembly process involving Ag^{I} under ammoniacal conditions and conforms that $[Ag(NH_3)_2]^+$-containing compounds are the intermediates during synthesis of some Ag^{I} coordination polymers.

Over the past decade, a renaissance has been devoted to the controlled synthesis of metallo-supramolecular species, such as finite coordination rings and cages and infinite coordination polymers, not only because of their intriguing structural diversity but also because of their potential as new functional materials.[1] Although thousands of functional coordination compounds have been successfully self-assembled, few details of the self-assembly process are well understood. As is well known, the reactions of Ag^{I} with multicarboxylates in aqueous solution often result in the formation of insoluble silver salts, presumably due to the fast coordination of the carboxylates to Ag^{I} cations to form polymers.[2] Hence, properly lowering the reaction speed, such as using ammoniacal conditions,[3] may result in the formation of crystalline products. Although Ag^{I} under ammoniacal conditions can form $\{[Ag(NH_3)_2]^+\}_n$ ($n = 1$ or 2)[4] which may slowly release the Ag^{I} cations along with escape of NH_3, they are stable and no transformations were found in them. So obtaining simultaneously intermediate and final compounds involving Ag^{I} under ammoniacal conditions is unprecedented. Recently, we have pursued a series of investigations into the self-assembly of Ag^{I} cation with different angular and linear bipodal N-donor ligands and multicarboxylates under ammoniacal conditions.[5] In an attempt to introduce versatile pyrazine-2,3-dicarboxylic acid[6] into above system, we simultaneously obtained the metastable compound $[Ag(NH_3)_2]$-$[Ag_3(pzdca)_2(NH_3)_4]$ (**1**) and the final stable compound $[Ag_2(pzdca)(H_2O)]_n$ (**2**) which is proved by X-ray diffraction to be the same as what has been reported by Chen et al.[7]

Compound **1** was obtained as needle-like colorless crystals by the reaction of Ag_2O and H_2pzdca in $H_2O/CH_3OH/NH_3$ media under ultrasonic treatment.[8] Crystals of **1** immersed in the mother liquor can transform to the documented block-like yellow crystals **2** in one day. The crystallographic analysis[9,10] reveals that **1** is a discrete complex composed of anion and cation the parts: $[Ag_3(pzdca)_2(NH_3)_4]^-$ (A) and $[Ag(NH_3)_2]^+$ (B). Each asymmetric unit contains three crystallographically independent Ag^{I} cations, of which Ag1 and Ag2 belong to part A and Ag3 belongs to part B, one pzdca anion and three coordinated NH_3 molecules. The coordination geometries of the Ag^{I} cations are completely different. Ag1 is coordinated with a T-shaped geometry by two NH_3 molecules and one O atom from pzdca. Ag2 and Ag3 locate on the inversion centers with half occupancy. Ag2 is coordinated with a rare square-planar geometry[11] by two N atoms and two O atoms from two symmetry-related pzdca anions. Ag3 involving an independent cation part B is linearly coordinated by two NH_3 molecules. The structure of **1** is not polymeric but a discrete one without consideration of supramolecular interactions (Figure 1). Both Ag–N and Ag–O bond lengths (Table S1)[10] are comparable with those in related compounds.[12]

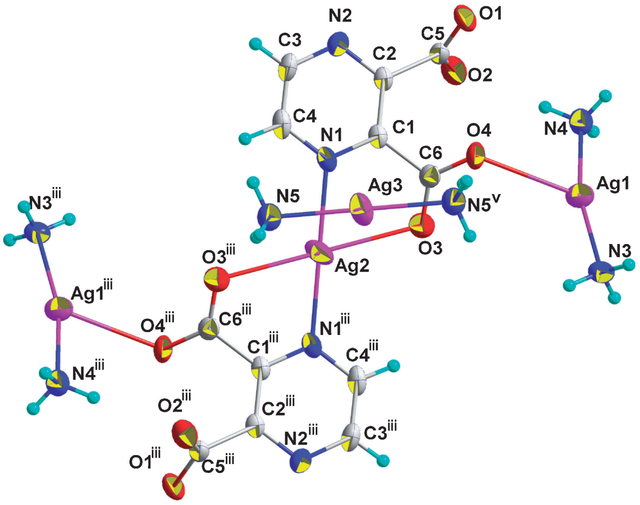


Figure 1. The structure of (I), showing the atom-numbering scheme and the coordination environment around the Ag(I) center. Displacement ellipsoids are drawn at 50% probability level. Hydrogen atoms are shown as small spheres of arbitrary radii (Symmetry codes: (iii) $-x+1$, $-y+1$, $-z+1$; (v) $-x+1$, $-y+1$, $-z$).

It is worthy to note that there are weak Ag···N and Ag···O interactions [Ag3···N1 = 3.049(4) and Ag1···O3 = 3.149(4) Å], both of which fall in the secondary bonding range (the sum of van der Waals radii of Ag and N(O) are 3.27 and 3.24 Å).[13] Between neighboring anion part A, as shown in Figure 2, the p···π interaction [$Cg1 \cdots Cg1^{x} = 3.329(3)$ Å; $Cg1$ is the centroid of the N1/C1/C2/N2/C3/C4 ring] and weak Ag···Ag interactions are coexistent. The abundant N–H···O hydrogen bonds between NH_3 and carboxylate groups (av. N3···O = 3.15 Å, ∠N3–H···O = 159°; N4···O = 3.10 Å, ∠N4–H···O = 164°; N5···O = 2.95 Å, ∠N5–H···O = 173°) combine the Ag···Ag and π···π interactions to stabilize the three-dimensional supramolecular framework of **1** (Figure S1)[10] (Symmetry codes: (i) x, $-y+1/2$, $z+1/2$; (iv) x, y, $z+1$; (x) $-x$, $-y+1$, $-z+1$; (ix) $-x$, $-y+1$, $-z$).

Keeping the needle-like colorless crystals **1** stay in the mother liquor for another day can convert them to block-like

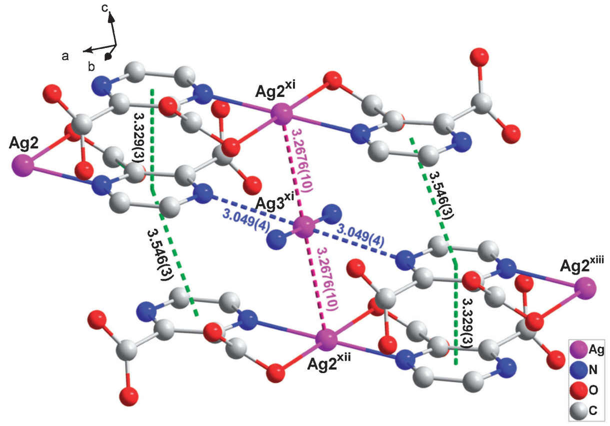
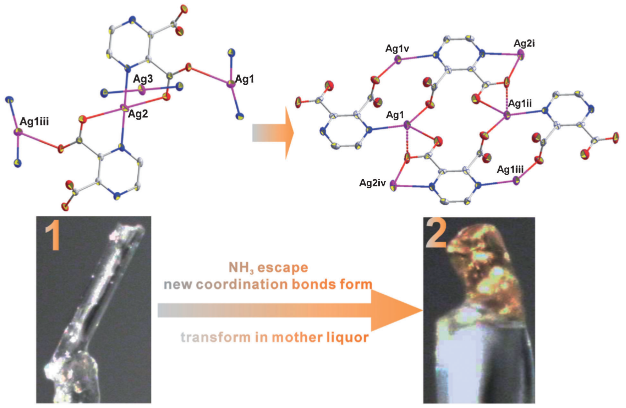


Figure 2. A ball-stick perspective view of supramolecular interactions including Ag···Ag, Ag···N, and $\pi\cdots\pi$ interactions in **1**. Hydrogen atoms have been omitted for clarity (Symmetry codes: (xi) $-1 + x, y, z$; (xii) $-1 + x, y, -1 + z$; (xiii) $-2 + x, y, -1 + z$).



Scheme 1. Schematic illustration of the transformation from **1** to **2** (Symmetry codes: (iii) $-x$, $1 - y$, $1 - z$ for **1**; (i) $-x$, $y + 0.5$, $1.5 - z$; (ii) $-x$, $1 - y$, $1 - z$; (iii) $x - 1$, y, $z - 1$; (iv) x, $0.5 - y$, $z - 0.5$; (v) $1 - x$, $1 - y$, $2 - z$, for **2**).

yellow crystals **2** (Scheme 1). This process is a spontaneous irreversible process and driven by the disassociation of $[Ag(NH_3)_2]^+$ along with new $Ag–N_{pzdca}$ bond formation. In **1**, the NH_3 molecules occupy the coordination sites of Ag^I and prevent Ag^I from binding to pzdca anions. The weak Ag···N interactions indicate that when Ag^I cation in $[Ag(NH_3)_2]^+$ entity becomes free, it prefers to coordinate with N_{pzdca} and then forms **2** which is a possible transformation route from **1** to **2**.

In summary, this study offers important information to in-depth understanding of the self-assembly process involving Ag^I cations under ammoniacal conditions and conforms that $[Ag(NH_3)_2]^+$-containing compounds are the intermediates during synthesis of some Ag^I coordination polymers.

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8 Synthesis of **1** and **2**: (**1**): A mixture of Ag_2O (116 mg, 0.5 mmol) and pyrazine-2,3-dicarboxylic acid (168 mg, 1 mmol) was added to a methanol–water solvent mixture (15 mL, 1:2 v/v) under ultrasonic conditions. An aqueous NH_3 solution (25%, 2 mL) was added dropwise to the mixture to give a clear solution. The resulting solution was left to evaporate slowly in the dark at room temperature for several weeks to give colorless needle-like crystals of **1**. The crystals were washed with deionized water and dried in air (yield: ca. 86%, based on Ag). Anal. Calcd. for $C_{12}H_{22}Ag_4N_{10}O_8$: C, 16.65; H, 2.56; N, 16.18%. Found: C, 16.60; H, 2.51; N, 16.26%. Selected IR peaks (cm^{-1}): 3410(s), 1630(s), 1560(vs), 1445(s), 1375(vs), 1223(m), 1116(w), 764(w), 729(m), 522(w); (**2**):**1** within mother liquor was left at room temperature. Over one day, yellow block **2**, clearly of distinctly different morphology to that of **1**, appeared in the mother liquor, and the crystals of **1** disappeared.

9 Structure parameters for **1** are available free of charge via Cambridge Crystallographic Data Centre under deposition numbers CCDC-750334 of **1**.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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