Self-assembly of Silver Triflate and 1,4-Bis(imidazol-1-yl) Xylene (bix) in the Presence of A Diphosphine: Discrete Metallomacrocycle Versus 2D Coordination Polymer*

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Abstract: Assembly of silver triflate with 1,4-bis(imidazol-1-yl) xylene in the presence of a diphosphine $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) provided complexes $[Ag_4(bix)_2(dppm)_4(CF_3SO_3)_2]$ (**1**) $(CF_3SO_3)_2 \cdot 2DMF \cdot 2H_2O$ and $[Ag(bix)(dppe)]_n$ (**2**) $(CF_3SO_3)_n \cdot nDMF \cdot nCH_3OH$, where the cation **1** is a discrete 34-membered metallomacrocycle and **2** a polymeric 2D (4,4) grid network. The backbone $(CH_2)_n$ of the diphsophine obviously plays the major role in the varied architectures.

Keywords: silver(Ⅰ) complex; 1,4-bis(imidazol-1-yl) xylene; diphosphine; crystal structure; ESI-MS
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Interests in metal-organic assemblies have been developed by leaps and bounds owing to the propensity of incorporating interesting functions such as catalytic, magnetic, electronic, and optical properties[1-3]. A plethora of composite organic/inorganic architectures, ranging from discrete molecular entities such as cages and metallomacrocycles to extended 1D, 2D, and 3D coordination polymers, have been reported. Though a completely rational design of such structures is not yet possible since there are so many factors such as the counter anion, solvent, temperature and the molar ratio of the precursor influencing the results, a rather effective strategy, the building-block approach[4,5], was put forward to partly solve the problem. Ditopic ligands with an arene core have been widely used as building blocks for constructing novel metal-organo-inorganic hybrid frameworks. For example, 1,4-bis(imidazol-1-yl) xylene (bix) has been reported to construct interpenetrating 2D or 3D coordination polymers[6-9]. It would be interesting to study the effect of the auxiliary ligand, such as diphosphines, which might be critical to the control of the shape and size of the molecular structures that formed. Herein, the construction of two nanosized complexes $[Ag_4(bix)_2(dppm)_4(CF_3SO_3)_2]$ (**1**) $(CF_3SO_3)_2 \cdot 2DMF \cdot 2H_2O$ and $[Ag(bix)(dppe)]_n$ (**2**) $(CF_3SO_3)_n \cdot nDMF \cdot nCH_3OH$ are reported.

1 Experimental

1.1 Synthesis

The ligand bix was synthesized according to the literature[6].

Complexes [**1**] $(CF_3SO_3)_2 \cdot 2DMF \cdot 2H_2O$ and [**2**] $(CF_3SO_3)_n \cdot nDMF \cdot nCH_3OH$ were prepared by a similar method: A solution of 0.1 mmol of bix·$2H_2O$ (0.027 g) in 5 mL of CH_3OH was added dropwise to a stirred solution of 0.1 mmol of $AgCF_3SO_3$ (0.026 g) in 5 mL of CH_3OH at room temperature. White precipitate formed immediately and the solution was filtered after stirring for 0.5 hr. The precipitate collected was then added with 5 mL of DMF, and then to the solution was added 0.1 mmol of diphosphine (dppm for **1** or dppe for **2**) with stirring for another 0.5 hr. It was filtered again and Et_2O was diffused into the filtrate slowly over several weeks at room temperature to give colorless cubic crystals of the product in 30% yield. Analyses calculate for $C_{69}H_{67}Ag_2F_6N_5O_8P_4S_2$ (**1**·$(CF_3SO_3)_2 \cdot 2DMF \cdot 2H_2O$) w/%: C, 51.41; H, 4.19; N, 4.34. Found: C, 51.69; H, 4.13; N, 4.18%. IR (cm^{-1}, KBr): 3 053, 1 482, 1 434, 1 270, 1 222, 1 148, 1 098, 1 029, 745, 696, 637. Analyses calculate for $C_{45}H_{49}AgF_3N_5O_5P_2S$(**2**·$(CF_3SO_3)_n \cdot nDMF \cdot nCH_3OH$) w/%: C, 54.12; H, 4.94; N, 7.01. Found: C, 54.77; H, 4.61; N, 7.34%. IR (cm^{-1}, KBr): 3 056, 1 510, 1 436, 1 264, 1 227, 1 154, 1 103, 1 080, 1 029, 731, 697, 636.

1.2 X-Ray Crystallography

Diffraction data of the single crystals of the complexes were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.071 073 nm). Absorption corrections

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were performed using the SADABS program.

The structures were solved by direct methods using the SHELXS-97 program and refined with SHELXL by full-matrix least-squares methods against F^2. Crystallographic data for **1**·$(CF_3SO_3)_2$·2DMF·$2H_2O$, triclinic, $P\bar{1}$, M_r=1612.02, a=1.339 8 (10), b=1.607 8 (12), c=1.743 7 (13) nm, α=79.512 (14)°, β=85.537 (13)°, γ=84.752 (13)°, V=3.671 (5) nm^3, Z=2, D_c=1.458 Mg/m^3, μ=0.748 mm^{-1}, R=0.060 1, wR=0.137 0. Crystallographic data for **2**·$(CF_3SO_3)_n$·nDMF·$n$$CH_3OH$, triclinic, $P\bar{1}$, M_r=998.76, a=1.185 0(5), b=1.421 9(6), c=1.487 9(6) nm, α=91.012(7)°, β=91.930(7)°, γ=112.393(6)°, V=2.315 5(17) nm^3, Z=2, D_c=1.433 Mg/m^3, μ=0.611 mm^{-1}, R=0.081 5, wR=0.235 8. Crystallographic data for **1**·2CF_3SO_3·2DMF·$2H_2O$ and **2**·$n$$CF_3SO_3$·$n$DMF·$n$$CH_3OH$ have been deposited with the cambridge crystallographic data center (CCDC No. 215680 and 236432).

2 Results and Discussion

As shown in Scheme 1, complexes **1**·$(CF_3SO_3)_2$·2DMF·$2H_2O$ and **2**·$(CF_3SO_3)_n$·nDMF·$n$$CH_3OH$ were prepared from the reaction of $AgCF_3SO_3$, bix·$2H_2O$ and diphosphines (dppm for **1** and dppe for **2**) in 1∶1∶1 molar ratio.

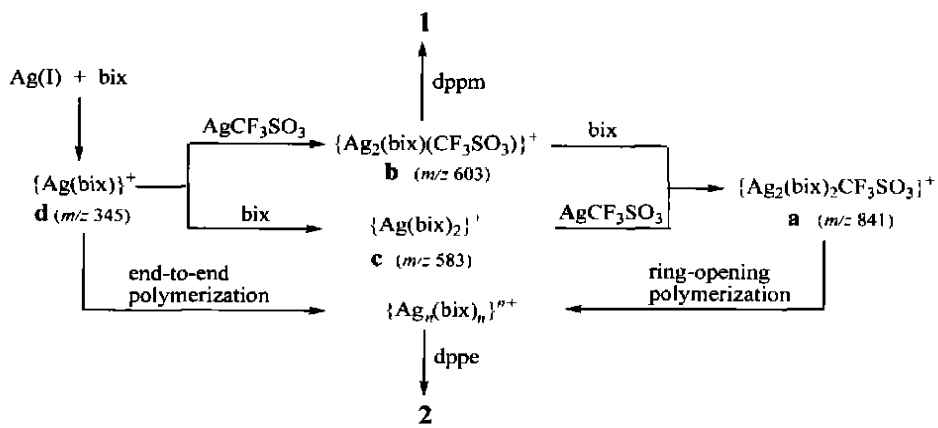
The formation processes of **1** and **2** can be elucidated by electrospray mass spectral analyses (ESI-MS). The precipitate in DMF collected from the reaction of bix·$2H_2O$ and $AgCF_3SO_3$ exhibits main peaks for the fragments $\{Ag_2(bix)_2(CF_3SO_3)\}^+$ (**a**, m/z 841, 100%), $\{Ag_2(bix)(CF_3SO_3)\}^+$ (**b**, m/z 603, 14%), $\{Ag(bix)_2\}^+$ (**c**, m/z 583, 27%) and $\{Ag(bix)\}^+$ (**d**, m/z 345, 62%).

The polymeric $\{Ag_n(bix)_n\}^{n+}$ chain in **2** could be formed either by the ring-opening polymerization of **a**[10] or by the end-to-end polymerization of **d**. After the addition of diphosphine, the assembly of the fragment **b** and dppm provided **1**, and that of the fragment $\{Ag_n(bix)_n\}^{n+}$ and dppe gave rise to **2**.

The structure of the cation $[Ag_4(bix)_2(dppm)_4(CF_3SO_3)_2]^{2+}$ **1** is shown in Fig. 1. A pair of dppm coordinated to two silver atoms Ag1 and Ag2 provides the ring unit $Ag_2(dppm)_2$ with the Ag…Ag distance of 0.343 2 nm, which is further bridged with the other unit $Ag_2(dppm)_2$ by two *anti*-conformational bix ligands to produce a 34-membered nanosized metallomacrocyclic $Ag_4C_{18}N_8P_4$ ring with the Ag…Ag distance across bix of 1.256 nm. Each Ag(Ⅰ) is tetrahedrally coordinated by P_2NO, with the two P atoms from two dppm, an N atom from one bix and an O from one $CF_3SO_3^-$. Each of the $CF_3SO_3^-$ anions weakly bridge two Ag(Ⅰ) ions in the $Ag_2(dppm)_2$ unit with Ag…O distances of 0.283 nm and 0.265 nm and is situated inside the nanoporous metallomacrocycle, thus stabilizing the molecular cavity.

The 2D cation $[Ag(bix)(dppe)]_n^{n+}$ **2** with each Ag(Ⅰ) tetrahedrally coordinated by P_2N_2 from two *anti*-dppe and two *anti*-bix as shown in Fig. 2, is formed by the crisscrossing polymeric chains $Ag_n(dppe)_n$ and $Ag_n(bix)_n$ with the Ag(Ⅰ) ions at the nodes in the shape of a (4, 4) grid sheet containing a series of 36-membered nanosized metallomacrocycles $Ag_4C_{20}N_8P_4$, with the Ag…Ag distance across the bix of 1.422 nm and that across the dppe of 0.738 or 0.762 nm (Fig. 3).

The two structures are shaped by different diphsophines. The dppm ligand with odd numbered backbone (n=1) is easy to doubly bridge two Ag(Ⅰ) atoms to form the closed $Ag_2(dppm)_2$ unit while the dppe ligand with even numbered backbone tends to link Ag(Ⅰ) atoms head-to-tail (singly bridges the Ag(Ⅰ)) to



Scheme 1 Formation processes of **1** and **2**

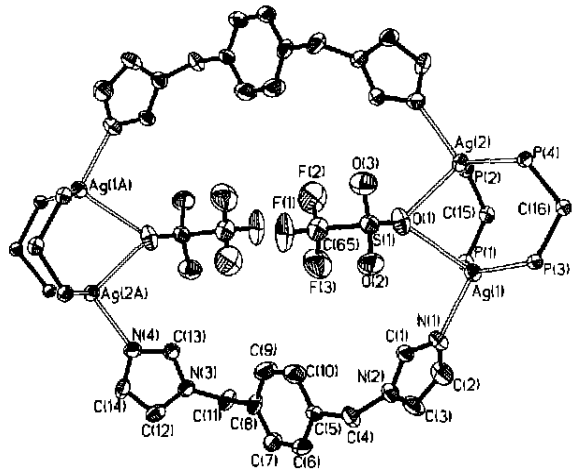


Fig. 1　View of the cation $[Ag_4(bix)_2(dppm)_4(CF_3SO_3)_2]^{2+}$ (**1**) with atomic labeling schecne.

The phenyl rings of dppm and hydrogen atoms were omitted for clarity. Selected atomic distances (nm) and bond angles (°): Ag1—N1 0.2363(8), Ag1—N2 0.2339(8), Ag1—O1 0.283(1), Ag1—O2 0.265(2), Ag1—P1 0.2481(3), Ag2—P2 0.2462(3), Ag1—P3 0.2455(3), Ag2—P2 0.2432(3), N1—Ag1—P3 11.19(2), Ni—Ag1—P1 10.06(2), P1—Ag1—P3 13.458(9), N4—Ag2—P4 11.407(18), P2—Ag2—P4 12.425(9)

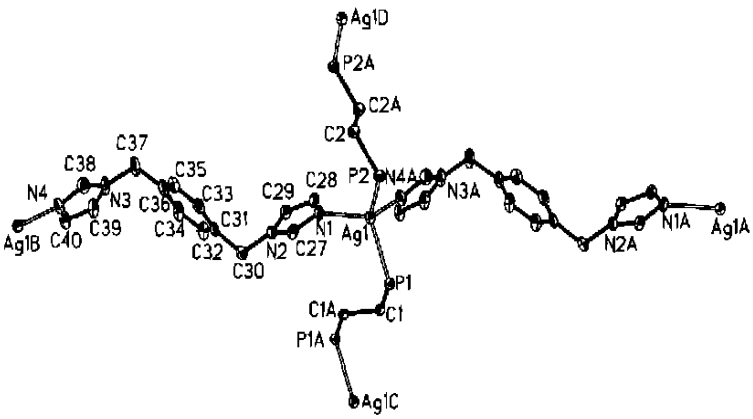


Fig. 2　View of a fragment of $[Ag(bix)(dppe)]_n^{n+}$ (**2**) with atomic labeling showing the metal coordination environment

The phenyl rings of dppe and hydrogen atoms were omitted for clarity. Selected atomic distances (nm) and bond angles (°): Ag1—N1 0.2334(7), Ag1—N4 0.2396(8), Ag1—P1 0.2489(2), Ag1—P2 0.2444(2), Ni—Ag1—N4 9.66(3), P1—Ag1—N4 9.73(2), P1—Ag1—P2 12.032(8), N1—Ag1—P2 11.54(2)

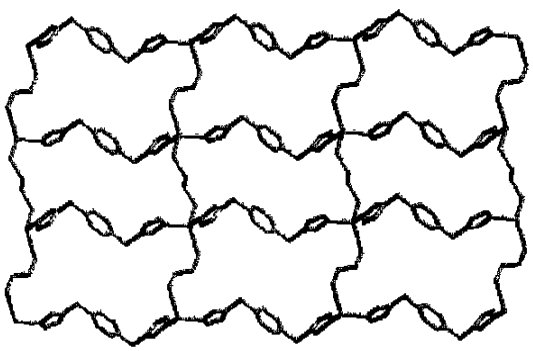


Fig 3　View of the 2D network of the cation $[Ag(bix)(dppe)]_n^{n+}$ (**2**)

form the polymeric $Ag_n(dppe)_n$ chain[11]. With the short backbone of dppm, the strong nucleophile $CF_3SO_3^-$ can loosely bridge the two Ag(Ⅰ) atoms in the $Ag_2(dppm)_2$ unit via one of the O atoms, thus favoring the formation of the discrete anion-stabilized tetranuclear metallomacrocycle $Ag_4(bix)_2(dppm)_4(CF_3SO_3)_2$ of **1**. However, with the longer backbone ($n=2$) of dppe, these functions are not favorable. The IR spectra also showed that the absorptions at 1 264 cm^{-1} for the free $CF_3SO_3^-$ anions are found in **2**, and those at 1 270 cm^{-1} for the partly coordinated $CF_3SO_3^-$ anions are found in **1**.

In summary, complexes of bix-Ag(Ⅰ) of different non-interpenetrating structures can be obtained by the mediation of a diphosphine as an auxiliary ligand. By suitable selection of auxiliary ligands, further investigation will be carried out to understand other assembly processes of transition metals with bix.

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三氟甲基磺酸银与 1, 4-二咪唑基二甲苯 (bix) 在双膦配体参与下的自组装: 零维金属大环配合物或二维配位聚合物

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摘 要: $AgCF_3SO_3$ 与 1, 4-二咪唑基-二甲苯 (bix) 在双膦配体 dppm 或 dppe 参与下通过自组装得到结构迥然不同的两个配合物: 零维金属大环配合物[Ag_4(bix)$_2$(dppm)$_4$(CF_3SO_3)$_2$]·(**1**)·$2CF_3SO_3$·2DMF·$2H_2O$ 及具有二维(4, 4)格子的聚合物[Ag(bix)(dppe)]$_n$·(**2**)·nCF_3SO_3·nDMF·$n$$CH_3OH$, 表明双膦配体的链上亚甲基的数目对配合物的结构有重要影响。

关键词: 银(Ⅰ)配合物; 1, 4-二咪唑基-二甲苯; 双膦配体; 晶体结构; 电喷雾—质谱

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