Synthesis and Structures of Silver(I) Adducts with 4-Amino-4*H*-1,2,4-triazole

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Reactions of silver(I) salts with 4-amino-4*H*-1,2,4-triazole (4-NH_2-tz) in a 1 : 1 molar ratio yield four new silver adducts, namely [Ag(4-NH_2-tz)](CF_3SO_3) (**1**), [Ag(4-NH_2-tz)$_{1.75}$](ClO_4) (**2**), [Ag(4-NH_2-tz)$_{1.75}$](BF_4) (**3**) and [Ag(4-NH_2-tz)$_{1.75}$](NO_3) (**4**). X-Ray analysis shows that **1** exhibits a 3D cationic $[Ag(4\text{-}NH_2\text{-tz})]^+$ metal-organic framework of **srs** topology; **2**, **3** and **4** are isostructural and display an infinite chain structure containing an Ag_4tz_6 cluster.

Key words: Silver, 4-Amino-4*H*-1,2,4-triazole, Adducts, Synthesis, Structure

Introduction

We recently embarked on an investigation of the structures of silver(I) adducts of 4-amino-3,5-disubstituted-4*H*-1,2,4-triazole (4-NH_2-3,5-R_2-tz), giving particular attention to the possible structural influence imparted by the anions or the 3,5-substituents of the triazole ring [1 – 3]. Several such complexes with different combinations of anions and substituents are known in the literature. For instance, when R is methyl, [Ag_2(4-NH_2-3,5-Me_2-tz)$_2$(CF_3COO)$_2$] [4], [Ag_2(4-NH_2-3,5-Me_2-tz)$_2$(C_6H_5COO)$_2$] · $2H_2O$ [5], [Ag_4(4-NH_2-3,5-Me_2-tz)$_6$](ClO_4)$_4$ · $4H_2O$, [Ag_4(4-NH_2-3,5-Me_2-tz)$_6$](CF_3SO_3)$_4$·$2H_2O$ [1], [Ag_4(4-NH_2-3,5-Me_2-tz)$_6$(CH_3CN)$_2$](CF_3SO_3)$_4$ · $2CH_3CN$ [3], [Ag_4(4-NH_2-3,5-Me_2-tz)$_6$][Ag_4(4-NH_2-3,5-Me_2-tz)$_6$(CH_3CN)$_2$](ClO_4)$_8$ · $2H_2O$ [6], and {[Ag_3(4-NH_2-3,5-Me_2-tz)$_2$(NO_3)$_2$](NO_3) · $2H_2O$}$_n$ [5] have been obtained and structurally characterized. When R is ethyl, the structures of [Ag_4(4-NH_2-3,5-Et_2-tz)$_6$](ClO_4)$_4$, [Ag_4(4-NH_2-3,5-Et_2-tz)$_6$](CF_3SO_3)$_4$, and {[Ag(4-NH_2-3,5-Et_2-tz)$_2$](ClO_4)}$_n$ have just been reported in one of our recent papers [1]. In a previous paper, we also described the structures of Ag(I) adducts with 4-NH_2-3,5-^{i}Pr_2tz, namely [Ag_2(4-NH_2-3,5-^{i}Pr_2-tz)$_2$(NO_3)$_2$(CH_3CN)], [Ag_3(4-NH_2-3,5-^{i}Pr_2-tz)$_3$](CF_3SO_3)$_3$, [Ag_4(4-NH_2-3,5-^{i}Pr_2-tz)$_6$](ClO_4)$_4$, and [Ag_4(4-NH_2-3,5-^{i}Pr_2-tz)$_6$](CF_3SO_3)$_4$ [2].

When we turned our attention to 4-amino-4*H*-1,2,4-triazole (4-NH_2-tz), the simplest form of 4-NH_2-3,5-R_2-tz, we were a little surprised to find that no Ag(I) adduct with 4-NH_2-tz has been studied by X-ray single crystal diffraction. An earlier paper reported the synthesis of the mononuclear adduct [Ag(4-NH_2-tz)$_2$]NO_3 in which the N^1 atom of triazole was proposed to be the donor based on IR spectroscopic data [7]. Schmidbaur *et al.* once reported the structure of a related complex, [Ag_2(tzH)$_2$(NO_3)$_2$], which features an Ag_2(N–N)$_2$ six-membered ring (tzH = 4*H*-1,2,4-triazole) [8]. In this paper, we report the synthesis and crystal structures of four Ag(I) complexes of 4-NH_2-tz with the anions being $CF_3SO_3^-$, ClO_4^-, BF_4^- and NO_3^-, respectively.

Results and Discussion

Synthesis

All the complexes were obtained in a straightforward method with the initial molar ratio of AgX and 4-NH_2-tz being 1 : 1. Interestingly, the molar ratio of Ag : tz in the final products is 1 : 1 (for X = $CF_3SO_3^-$) and 1 : 1.75 (for X = BF_4^-, ClO_4^-, NO_3^-), respectively, based on elemental analyses and X-ray diffraction studies. In the case of NO_3^-, we also isolated colorless needles with an Ag : tz ratio of 1 : 1.25 from the same solution. However, the quality of the crystals was poor and thus not suitable for X-ray diffraction studies. It is noteworthy that the Ag : tz = 1:2 adduct, Ag(4-NH_2-tz)$_2$$NO_3$, has been prepared by using an initial Ag : tz ratio of 1 : 3 [7].

Crystal structures

[Ag(4-NH_2-tz)](CF_3SO_3) (**1**) crystallizes in the orthorhombic space group $P2_12_12_1$ and exhibits a 3D

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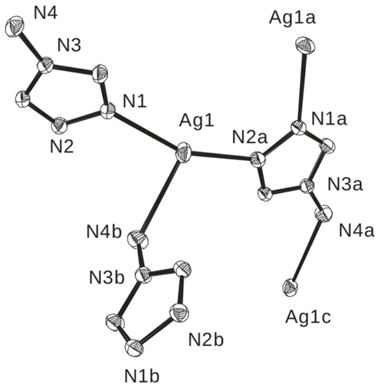

Fig. 1a. ORTEP diagram (35 % probability) of a fragment of the 3D cationic $[Ag(4\text{-}NH_2\text{-tz})]^+$ MOF in **1** with atom labels, showing the coordination geometries around Ag1 and the coordination mode of the $4\text{-}NH_2$-tz ligand. Symmetry code: a) $x + 1/2$, $-y + 3/2$, $-z$; b) $-x + 3/2$, $-y + 1$, $z - 1/2$; c) $-x + 2$, $y + 1/2$, $-z - 1/2$. Selected bond lengths (Å) and angles (deg): Ag1–N2a 2.226(3), Ag1–N1 2.248(3), Ag1–N4b 2.587(4); N2a–Ag1–N1 152.69(13), N2a–Ag1–N4b 115.99(13), N1–Ag1–N4b 88.81(13).

metal-organic framework (MOF). The asymmetric unit consists of one Ag(I) cation, one $4\text{-}NH_2$-tz molecule and one uncoordinated $CF_3SO_3^-$ anion. The Ag(I) atom is coordinated by two triazole N^1(or N^2) atoms and one amino N atom in a distorted T-shape; $4\text{-}NH_2$-tz serves as μ_3-N^1,N^2,N(amino) bridge (Fig. 1). The bond lengths of Ag–N(tz) are much shorter than that of Ag–N(amino) (2.226(3), 2.248(4) Å *vs*. 2.587(4) Å). Coordination of an amino group attached to an azole ring is known for a few reported Ag-azole complexes [9, 10].

Pairs of Ag atoms are linked by $4\text{-}NH_2$-tz bridges exploiting their N^1, N^2 atoms, leading to 2_1 infinite helices extending parallel to the *a* axis. It is noteworthy that all the helices in the crystal are of the same handedness. Further connection of the helices *via* Ag–N(amino) bonds gives rise to the 3D cationic $[Ag(4\text{-}NH_2\text{-tz})]^+$ MOF (Fig. 1b). This MOF possesses 1D channels along the *a* or *c* axes, in which the $CF_3SO_3^-$ anions suit. Hydrogen bonds involving the O atom of $CF_3SO_3^-$ and the amino group of $4\text{-}NH_2$-tz might also contribute to the formation of the present structure ($N4\cdots O2^i$ 2.946(4) Å; *i*: $-x + 2$, $y + 1/2$, $-z + 3/2$).

From a topological point of view, the Ag cation and the triazole molecule can be regarded as three-connected nodes. The structure of the cationic $[Ag(4\text{-}NH_2\text{-tz})]^+$ MOF can be simplified to a **srs** net, which is also well known as a (10,3)-a net according to Wells' nomenclature [11]. It should be pointed out that the **srs** net is uninodal, that is to say, the nodes derived from the Ag cation and the triazole molecule are the same in the topological study of this complex.

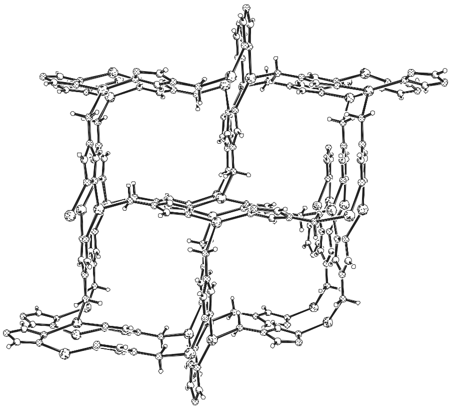

Fig. 1b. Packing diagram of the 3D cationic $[Ag(4\text{-}NH_2\text{-tz})]^+$ MOF viewed along the *a* axis. $CF_3SO_3^-$ anions (not shown) are located in the channels.

$[Ag(4\text{-}NH_2\text{-tz})_{1.75}](ClO_4)$ (**2**) crystallizes in space group *C*2/*c* and exhibits an infinite chain structure. The asymmetric unit consists of two Ag(I) cations, three whole and one-half $4\text{-}NH_2$-tz ligands, and two uncoordinated ClO_4^- anions. The Ag(I) atom is either triangularly (Ag1) or tetrahedrally (Ag2) coordinated

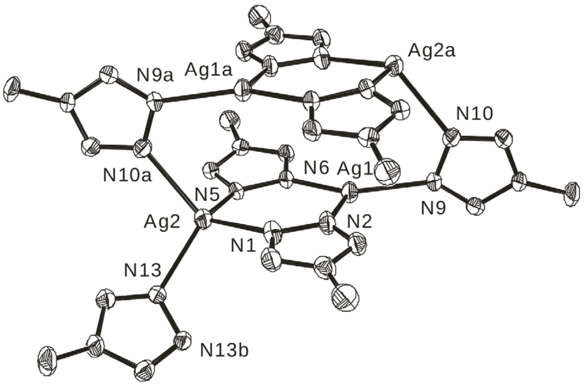

Fig. 2a. ORTEP diagram (35 % probability) of a fragment of the 1D $[Ag(4\text{-}NH_2\text{-tz})_{1.75}]_n^{n+}$ chain in **2** with atom labels, showing the Ag_4tz_6 cluster and the coordination geometries around Ag1 and Ag2 atoms. Symmetry code: a) $-x + 2$, $-y$, $-z + 1$; b) $-x + 2$, y, $-z + 1/2$. Selected bond lengths (Å) and angles (deg): Ag1–N6 2.179(4), Ag1–N9 2.200(4), Ag1–N2 2.314(5), Ag2–N13 2.283(4), Ag2–N5 2.283(4), Ag2–N1 2.326(5), Ag2–N10a 2.369(4); N6–Ag1–N9 142.44(16), N6–Ag1–N2 114.77(15), N9–Ag1–N2 102.46(15), N13–Ag2–N5 133.04(16), N13–Ag2–N1 94.11(16), N5–Ag2–N1 110.09(15), N13–Ag2–N10a 104.85(15), N5–Ag2–N10a 98.81(16), N1–Ag2–N10a 117.41(16).

Table 1. Crystal data for **1** – **4**.

	1	**2**	**3**	**4**
Formula	$C_3H_4AgF_3N_4O_3S$	$C_7H_{14}Ag_2Cl_2N_{14}O_8$	$C_7H_{14}Ag_2B_2F_8N_{14}$	$C_7H_{14}Ag_2N_{16}O_6$
M_r	341.03	708.96	683.68	634.08
Crystal size, mm^3	0.30 × 0.27 × 0.19	0.20 × 0.16 × 0.16	0.24 × 0.22 × 0.20	0.22 × 0.21 × 0.20
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$C2/c$	$C2/c$
a, Å	8.034(2)	21.362(4)	21.125(4)	21.031(4)
b, Å	9.747(3)	14.540(3)	14.387(3)	14.021(3)
c, Å	11.272(2)	13.349(3)	13.278(3)	13.123(3)
β, deg	90	91.49(3)	92.15(3)	102.85(3)
V, Å^3	882.7(4)	4144.7(14)	4032.8(14)	3772.9(13)
Z	4	8	8	8
T, K	298(2)	298(2)	298(2)	298(2)
D_{calcd}, Mg m^{-3}	2.57	2.27	2.25	2.23
μ, mm^{-1}	2.6	2.2	2.0	2.1
$F(000)$, e	656	2768	2640	2480
hkl range	$-10 \le h \le 10$, $-12 \le k \le 12$, $-12 \le l \le 14$	$-27 \le h \le 15$, $-15 \le k \le 18$, $-17 \le l \le 17$	$-28 \le h \le 28$, $-19 \le k \le 19$, $-18 \le l \le 17$	$-28 \le h \le 28$, $-19 \le k \le 19$, $-17 \le l \le 17$
Refl. coll. / unique / R_{int}	6532 / 1978 / 0.0222	7785 / 4527 / 0.0274	26710 / 5421 / 0.0323	24925 / 5076 / 0.0359
Param. refined	136	304	304	294
Final $R1$ / $wR2$ [$I \ge 2\sigma(I)$]	0.0259 / 0.0664	0.0476 / 0.0992	0.0563 / 0.1379	0.0557 / 0.1110
Flack x parameter	0.03(4)	–	–	–
GoF (F^2)	1.071	1.096	1.167	1.181
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.87 / −0.62	0.55 / −0.56	1.00 / −1.14	0.72 / −0.76

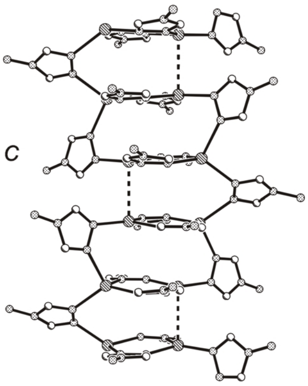

Fig. 2b. A view of the 1D $[Ag(4\text{-}NH_2\text{-}tz)_{1.75}]_n{}^{n+}$ chain in **2**. The dashed lines represent the argentophilic interactions.

by triazole N^1(or N^2) atoms with the Ag–N distances falling in the range of 2.179 (4) – 2.369 (4) Å (Fig. 2a). 4-NH_2-tz acts as μ_2-N^1,N^2 bridge; the amino group does not participate in the coordination.

To understand this structure, firstly we consider the Ag_2tz_2-subunit featuring an $(Ag–N–N\text{-})_2$ ring (Ag1, Ag2, N1, N2, N5, N6), which is rather common in metal-azole chemistry. Two parallel Ag_2tz_2 subunits, related by an inversion center, are linked by another two 4-NH_2-tz ligands from the waist to give rise to an Ag_4tz_6 cluster (Fig. 2a). Formation of the Ag_4tz_6 cluster has been observed in several silver(I)-triazole complexes; the effect of 3,5-substituents of the triazole on the structure of the Ag_4tz_6 cluster has been discussed in our previous paper [1]. The Ag_4tz_6 clusters are further linked *via* the 4-NH_2-tz ligands at Ag2 to form infinite chains running along the *c* axis. As shown in Fig. 2b, the presence of argentophilic interactions might also contribute to the formation of the chain of $[Ag(4\text{-}NH_2\text{-}tz)_{1.75}]_n{}^{n+}$ (Ag1···Ag1^i = 3.156(1) Å; i: $-x + 2, y, -z + 1/2$) [12].

$[Ag(4\text{-}NH_2\text{-}tz)_{1.75}](BF_4)$ (**3**) and $[Ag(4\text{-}NH_2\text{-}tz)_{1.75}](NO_3)$ (**4**) are isostructural with **2** and will not be discussed here.

Experimental Section

4-Amino-1,2,4-triazole was prepared according to the published method [13]. Other reagents were commercially available and used as received without further purification.

Infrared spectra were obtained from KBr pellets on a Bruker Vector 22 FT-IR spectrometer. The CHN microanalyses were carried out with a Carlo Erba 06 elemental analyzer. ^{1}H NMR spectra were recorded with a Bruker DPX-400 spectrometer (400 MHz).

*[Ag(4-NH$_2$-tz)](CF$_3$SO$_3$) (**1**)*

A solution of $AgCF_3SO_3$ (0.15 mmol, 8.5 mg) in CH_3CN (2 mL) was mixed with 2.5 mL of an ethanol solution of 4-NH_2-tz (0.15 mmol, 12.6 mg). The resulting mixture was allowed to evaporate for about two weeks to yield colorless blocks of **1** suitable for X-ray work. Yield: 73 %. – $C_3H_4AgF_3N_4O_3S$ (341.02): calcd. C 10.57, H 1.18, N 16.43; found C 10.64, H 1.18, N 15.98. – IR (KBr pellet): ν = 3349 w, 1633 w, 1258 s (-CF_3), 1164 s, 1038 s, 644 s, 520 m cm^{-1}.

*[Ag(4-NH$_2$-tz)$_{1.75}$](ClO$_4$) (**2**)*

$AgClO_4$ (21.7 mg, 0.1 mmol) and 4-NH_2-tz (0.1 mmol, 8.5 mg) were mixed in 2 mL of CH_3CN. Ether was allowed to diffuse slowly into the resulting solution to afford, within several days, colorless needles of **2** in 70 % yield. – $C_{3.5}H_7N_7AgO_4$ (354.46): calcd. C 11.86, H 1.99, N 27.66; found C 11.47, H 1.55, N 27.65. – IR (KBr pellets): ν = 3308 w, 1626 s, 1526 m, 1385 m, 1193 s, 1087 s (ClO_4^-), 863 w, 622 s cm^{-1}. – ^1H NMR (D_2O): δ = 8.49 (s, 2H, 3,5-tz) ppm.

*[Ag(4-NH$_2$-tz)$_{1.75}$](BF$_4$) (**3**)*

This complex was prepared in a similar way as that for **2**, using $AgBF_4$ instead of $AgClO_4$. Yield: 75 %. – IR (KBr pellet): ν = 3317 w, 1629 m, 1527 w, 1077 s (BF_4^-), 864 w, 620 s cm^{-1}. – ^1H NMR (CD_3CN): δ = 8.37 (s, 2H, 3,5-tz) ppm.

*[Ag(4-NH$_2$-tz)$_{1.75}$](NO$_3$) (**4**)*

$AgNO_3$ (5.1 mg, 0.03 mmol) and 4-NH_2-tz (2.6 mg, 0.03 mmol) were mixed in 3 mL of CH_3CN; the resulting solution was allowed to evaporate for two days to yield colorless prisms, suitable for X-ray work. Yield: 10 %.

X-Ray crystal structure determination

Diffraction intensities were collected on a Bruker SMART 1K CCD diffractometer (for **1**), a Rigaku RAXIS-IV IP diffractometer (for **2**) and a Rigaku Saturn 724 CCD diffractometer (for **3** and **4**), with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Absorption corrections were applied by using the MULTISCAN program. The structures were solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXS-97 and SHELXL-97 programs, respectively [14]. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically. The crystallographic data are listed in Table 1.

CCDC 743386–743389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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