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Anion-Dependent Structural Diversity in Silver(I) Complexes of 4-Amino-3,5-diisopropyl-1,2,4-triazole

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Reactions of silver salts with 4-amino-3,5-diisopropyl-1,2,4-triazole (L) afford dinuclear complex $[Ag_2L_2(NO_3)_2(CH_3CN)]$, triangular complex $[Ag_3L_3](CF_3SO_3)_3$, and cyclic tetranuclear complexes $[Ag_4L_6](BF_4)_4$ and $[Ag_4L_6](ClO_4)_4$. On the basis of the X-ray analyses, anions are found to play an important role in determining the structures. Through coordination/noncoordination, anions can impart their influence on the coordination geometry of Ag atoms and the angles of N–Ag–N, which seems to be the main factor controlling the nuclearity of the reaction products in this system. ^{1}H NMR and MS measurements suggest that these complexes probably retain their structural integrities in CH_3CN solution.

Introduction

With the coordination complexes of metals, the anions serve more than merely balancing the charges of a cationic species;[1–8] anions impart their influence on the structure of a given supramolecular system through coordinative bonding to metal ions or through weak interaction with organic ligands. Leob et al. reported that a molecular square, rectangle and an infinite helical chain have been obtained by the reaction of 4-(2-pyridyl)pyrimidine with various silver salts and the degree of aggregation is dependent on the anion used.[2] Dunbar et al. found that reaction of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine with first-row transition metals could yield a molecular square and a pentagon with one anion accommodated in the cavities of the polygons. In this case, anions function as templates through anion-π interactions.[3] It seems promising that one can, to some extent, control or tune the structures of some supramolecules by simply changing anions. Obviously, before the use of anions can become a powerful tool for synthetic chemists in the construction of supramolecules, more work is needed towards understanding the mechanism of anion action.

Recent years have seen a rapidly increasing interest in the structures and properties of metal complexes of 1,2,4-triazole and its derivatives.[9] 1,2,4-Triazole is believed to unite the coordination geometries of both pyrazoles and imidazoles, and exhibit versatile coordination modes upon ligation to metals. 4-Amino-3,5-diisopropyl-1,2,4-triazole (4-NH_2-3,5-$i$$Pr_2$-tz) has been known for some time,[10] however, so far only few of its metal complexes have appeared in the literature to the best of our knowledge.[11] On the other hand, the less-crowded analogues with methyl or ethyl groups in place of the isopropyl groups are common ligands that furnish a large number of adducts with metal salts.[9] We report herewith the syntheses and crystal structures of four Ag^I-4-NH_2-3,5-$i$$Pr_2$-tz complexes; the structural outcomes of these adducts appear to be dependent on the nature of anions used.

Results and Discussion

Structure of $[Ag_2(\mu_2\text{-}4\text{-}NH_2\text{-}3,5\text{-}i Pr_2\text{-}tz)_2(NO_3)_2(CH_3CN)]$ (1)

The product of stoichiometric quantities of $AgNO_3$ and 4-NH_2-3,5-$i$$Pr_2$-tz is the dinuclear complex **1**; the two Ag atoms are four-coordinate in different environments (Figure 1). The Ag(1) atom is coordinated by two triazole N atoms, two O atoms from the chelating nitrate, while the Ag(2) atom is coordinated by two triazole N atoms, one N atom of acetonitrile, and one O atom from the monodentate nitrate; each triazole bridges two Ag atoms (Scheme 1, a). The distance between Ag(1) and Ag(2) is 3.2867(5) Å, less than the sum of the van der Waals radii for the Ag atoms (3.44 Å). Complex **1** features a $(Ag–N–N–)_2$ ring having a boat conformation with the two Ag atoms forming the ring tips. Such a six-membered ring is also observed in other (triazole)silver complexes, e.g. $[Ag_2(\mu_2\text{-tzH})_2(NO_3)_2]$[15] and $[Ag_2(\mu_2\text{-}4\text{-}NH_2\text{-}3,5\text{-}Me_2\text{-tz})_2(CF_3COO)_2]$[16] (tzH = 1,2,4-triazole; 4-NH_2-3,5-Me_2-tz = 4-amino-3,5-dimethyl-1,2,4-triazole). A number of dinuclear pyrazolato complexes also have this feature.[17,18]

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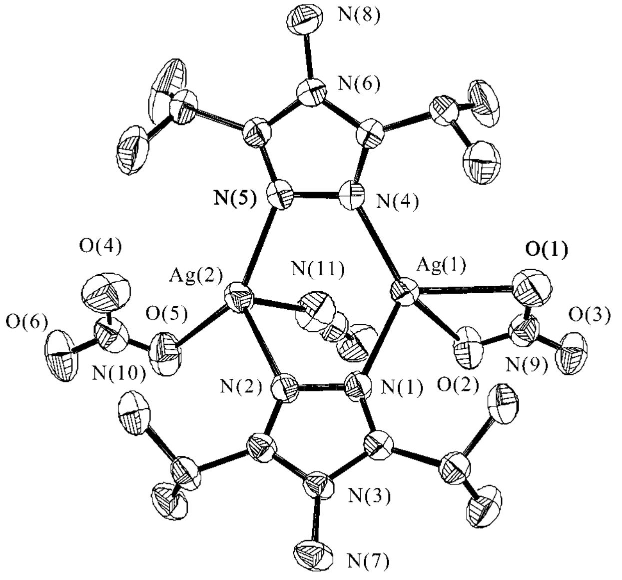
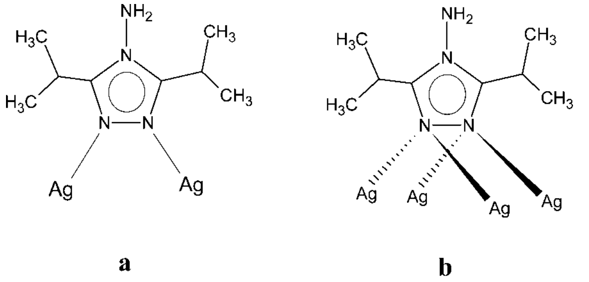


Figure 1. ORTEP diagram (at 35% probability) of the X-ray structure of [Ag$_2$(μ_2-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_2$(NO$_3$)$_2$(CH$_3$CN)] (**1**). Selected distances [Å] and angles [°]: Ag(1)···Ag(2) 3.2867(5), Ag(1)–N(1) 2.282(3), Ag(1)–N(4) 2.213(3), Ag(1)–O(1) 2.567(4), Ag(1)–O(2) 2.471(3), Ag(2)–N(2) 2.325(3), Ag(2)–N(5) 2.275(3), Ag(2)–N(11) 2.526(5), Ag(2)–O(5) 2.507(4), N(1)–Ag(1)–N4 110.56(11), N(2)–Ag(2)–N(5) 109.88(11), N(2)–N(1)–Ag(1) 113.4(2), N(1)–N(2)–Ag(2) 115.0(2), N(5)–N(4)–Ag(1) 116.6(2), N(4)–N(5)–Ag(2) 113.0(2).



Scheme 1.

From the structure of **1**, we can see that nitrates participate in the distorted four-coordinate environment around the Ag atoms, the N–Ag–N angles of ca. 110° are critical for the formation of the six-membered ring. For a given system like this one containing silver(I) and an *exo*-bidentate ligand, other cyclic products or 1D complexes might be formed,[19] depending on the angles of N–Ag–N. It is thus possible to obtain other products by using weaker coordinating or noncoordinating anions, which would have an influence on the coordination geometry of Ag atoms and the angles of N–Ag–N.

Structure of [Ag$_3$(μ_2-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_3$](CF$_3$SO$_3$)$_3$ (2)

Trifluoromethylsulfonates are weaker coordinating anions than nitrates owing to the electron-withdrawing CF$_3^-$ entity. In the AgCF$_3$SO$_3$ adduct, **2**, the (Ag–N–N–)$_n$ ring is a nine-membered, triangular-shaped ring. The Ag atoms are two-coordinate in a linear geometry, and the triazoles act as *exo*-bidentate bridging ligands (see parts a in Figure 2 and Scheme 1). The (Ag–N–N–)$_3$ ring is roughly planar, the mean deviation from the plane defined by three Ag atoms and six triazole N atoms being 0.0853 Å.

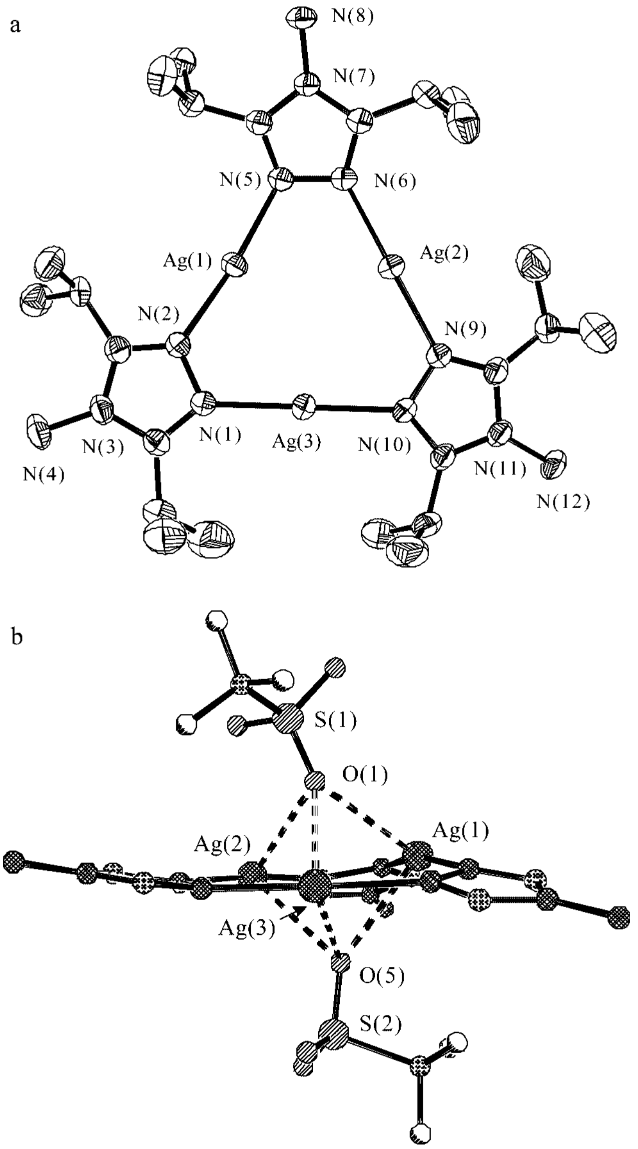


Figure 2. (a) ORTEP diagram (at 35% probability) of the X-ray structure of the cationic triangular [Ag$_3$(μ_2-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_3$]$^{3+}$ in **2**. (b) An edge-on-view with the two closest anions of CF$_3$SO$_3^-$. Selected distances [Å] and angles [°]: Ag(1)···Ag(2) 3.4316(9), Ag(1)···Ag(3) 3.4579(8), Ag(2)···Ag(3) 3.5573(8), Ag(1)–N(2) 2.132(3), Ag(1)–N(5) 2.129(3), Ag(2)–N(6) 2.159(3), Ag(2)–N(9) 2.168(3), Ag(3)–N(1) 2.165(3), Ag(3)–N(10) 2.168(3), N(5)–Ag(1)–N(2) 165.36(14), N(6)–Ag(2)–N(9) 176.02(14), N(1)–Ag(3)–N(10) 178.72(14), N(1)–N(2)–Ag(1) 121.5(2), N(6)–N(5)–Ag(1) 119.4(2), N(5)–N(6)–Ag(2) 117.8(2), N(10)–N(9)–Ag(2) 119.6(2), N(2)–N(1)–Ag(3) 116.3(2), N(9)–N(10)–Ag(3) 120.4(2).

Two of the three CF$_3$SO$_3^-$ anions are located on each side of the (Ag–N–N–)$_3$ ring with one O atom pointing to the centre of the triangle defined by three Ag atoms; contacts are O(1)···Ag(1) 2.668 Å, O(1)···Ag(2) 2.711 Å, O(1)···Ag(3) 2.742 Å, O(5^i)···Ag(1) 2.696 Å, O(5^i)···Ag(2)

2.736 Å, O(5^i)···Ag(3) 2.684 Å (symmetry code: *i*: –*x*, –*y* + 1, –*z* + 1) (Figure 2, b). Interestingly, while the above-mentioned two weakly coordinated $CF_3SO_3^-$ anions are in full occupancy in the X-ray structure, the third one, which has no contacts with Ag atoms, is disordered and has been refined as two parts with an occupancy factor of 0.5 each. Since the structure motif of the 1D chain may compete with the triangle when the angular units of ca. 60° (the triazole ligand) are combined with the ditopic linear units (the two-coordinate Ag^I atoms),[19] the triangular arrangement observed in **2** is possibly the result of the pre-organization of the Ag atoms and triazoles through weak Ag···O interactions.

A number of neutral triangular silver-pyazolates have been known for a long time,[20] however, a triangular silver-triazole compound has not been reported; on the other hand several Pd^{II}, Cu^{II}-triazole compounds do adopt this triangular motif.[21]

Structures of $[Ag_4(\mu_2\text{-4-NH}_2\text{-3,5-}i\text{Pr}_2\text{-tz})_6](ClO_4)_4\cdot H_2O$ (3) and $[Ag_4(\mu_2\text{-4-NH}_2\text{-3,5-}i\text{Pr}_2\text{-tz})_6](BF_4)_4$ (4)

Since two different anions (NO_3^- and $CF_3SO_3^-$) give two different structures of silver complexes of 4-NH_2-3,5-*i*Pr_2-tz, the possibility exists that other structural arrangements may be discovered in this system when other anions with different shapes and different coordinating abilities are used. Perchlorate and tetrafluoroborate anions have been proven to be weaker or noncoordinate ligands for silver(I), therefore $AgClO_4$ and $AgBF_4$ were used in the reaction with 4-NH_2-3,5-*i*Pr_2-tz. X-ray analyses demonstrate that the resulting two new compounds **3** and **4** are structurally similar, however, different from **1** and **2**. They are tetranuclear compounds with the formula $Ag_4L_6X_4$, featuring a $(Ag–N–N–)_4$ ring (L = 4-NH_2-3,5-*i*Pr_2-tz; X = ClO_4^-, BF_4^-). Figure 3 shows the structure of compound **3**. In both complexes the four Ag atoms are approximately coplanar defining a rhombus with Ag–Ag distances in the range of 3.374(1)–3.444(1) Å in **3** and 3.303(1)–3.477(1) Å in **4**, Ag–Ag–Ag angles of 88.02(2)–88.77(2)° in **3** and 86.93(2)–93.00(2)° in **4**. The Ag_4 rhombus in **3** is actually a little butterfly-distorted while that in **4** is almost planar, as indicated by the mean deviations of Ag atoms from the best-fit Ag_4 planes being 0.2823 Å (for **3**) and 0.0460 Å (for **4**). For both, the four bridging triazole ligands alternate above and below the Ag_4-plane forming a $(Ag–N–N–)_4$ ring of roughly S_4 symmetry (Scheme 1, a). The best-fit planes of the opposite triazoles form dihedral angles of 46.0, 54.0° and 30.5, 53.9° for **3** and **4**, respectively. A similar $(Ag–N–N–)_4$ ring is observed in the pyrazole complex $[Ag(\mu_2\text{-3,5-}t\text{Bu}_2\text{pz})]_4$,[22] however, the rings in **3** and **4** are flatter than that in $[Ag(\mu_2\text{-3,5-}t\text{Bu}_2\text{pz})]_4$. Additionally, two triazole ligands are placed nearly orthogonally on each side of the Ag_4 plane with the Ag···N contacts falling in the range of 2.513(5)–2.845(5) Å (for **3**) and 2.428(5)–2.859(5) Å (for **4**). These values are much longer than the Ag–N distances of the $(Ag–N–N–)_4$ rings, thus these two triazoles are only weakly bound to Ag atoms in an uncommon η^2,η^2,μ_4 fashion (Scheme 1, b).

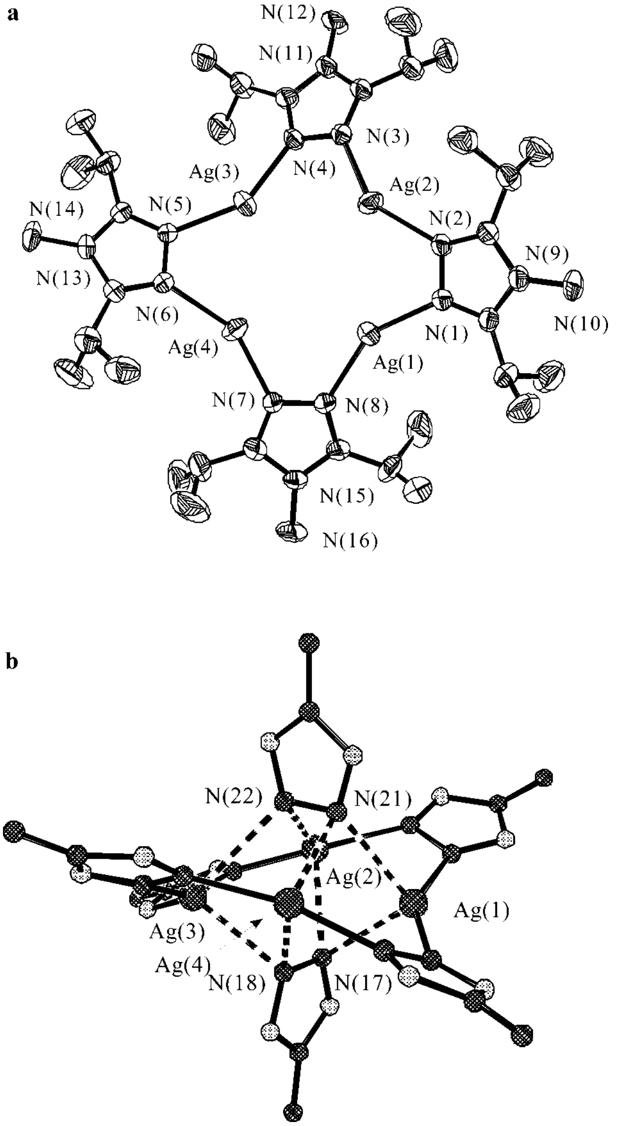


Figure 3. (a) ORTEP diagram (at 35% probability) of the X-ray structure of the cationic tetranuclear ring $[Ag_4(\mu_2\text{-4-NH}_2\text{-3,5-}i\text{Pr}_2\text{-tz})_4]^{4+}$ in **3**. (b) A side view of $[Ag_4(\mu_2\text{-4-NH}_2\text{-3,5-}i\text{Pr}_2\text{-tz})_6]^{4+}$ in **3** showing two weakly bound triazoles (the isopropyl groups are omitted for clarity). Selected distances [Å] and angles [°]: Ag(1)···Ag(2) 3.3754(9), Ag(3)···Ag(4) 3.3743(9), Ag(2)···Ag(3) 3.4436(9), Ag(1)···Ag(4) 3.4399(9), Ag(1)–N(1) 2.220(5), Ag(1)–N(8) 2.240(5), Ag(2)–N(3) 2.206(5), Ag(2)–N(2) 2.238(5), Ag(3)–N(5) 2.190(5), Ag(3)–N(4) 2.204(5), Ag(4)–N(7) 2.186(5), Ag(4)–N(6) 2.198(5), Ag(1)···N(17) 2.570(5), Ag(1)···N(21) 2.626(5), Ag(2)···N(22) 2.513(5), Ag(2)···N(17) 2.678(5), Ag(3)···N(18) 2.555(5), Ag(3)···N(22) 2.845(5), Ag(4)···N(21) 2.621(5), Ag(4)···N(18) 2.768(5), N(1)–Ag(1)–N(8) 148.80(18), N(3)–Ag(2)–N(2) 147.04(18), N(5)–Ag(3)–N(4) 148.91(18), N(7)–Ag(4)–N(6) 149.99(18).

Considering all the close contacts, the coordinate geometry of Ag atoms is better described as highly distorted tetrahedral. The N–Ag–N angles in $(Ag–N–N–)_4$ rings fall in the range of 146.4(2)–157.6(2)°. These values are less than those in $(Ag–N–N–)_3$ (ca. 180°), but larger than those in $(Ag–N–N–)_2$ (ca. 110°), which might account for the formation of the $(Ag–N–N–)_4$ ring in **3** and **4**. Very recently, Ag-triazole complexes with the same formula of $Ag_4L_6X_4$ have been reported by Cheng et al.[23] Interestingly, their complexes could be considered as two dinuclear units (similar to that in **1**), which are further connected via two additional N^1,N^2-bridged triazoles and therefore are structurally different from those we report in this paper.

Hydrogen bonds are found in the crystal structures of the four complexes. In complexes **1**, **2** and **4**, some of the amino groups of the triazole ligands serve as donors and the O atoms and/or F atoms of anions as acceptors for the hydrogen bonds. In **3**, only one amino group [N(24)] is found to form a hydrogen bond with the lattice water molecule [O(17)]; the water molecule is further H-bonded with two O atoms [O(2), O(13)] from two perchlorates. Therefore, this water molecule acts as both acceptor and donor in the hydrogen bonds presenting in **3**. The distances of N(24)···O(17), O(17)···O(2) and O(17)···O(13) are 2.846(13), 2.977(15) and 2.763(19) Å, respectively. The hydrogen bonds observed here, although relatively weaker, might contribute to the stabilisation and packing of the molecules in the crystals.

Solution Study

Free 4-NH_2-3,5-*i*Pr_2-tz exhibits resonances of *i*Pr protons at δ = 3.15 [m, H-C(Me)$_2$] and 1.27 (d, Me) ppm in CD_3CN; complexes **1**–**4** show only one set of slightly downfield-shifted resonances for the corresponding *i*Pr protons at 3.28, 1.32 (**1**); 3.25, 1.32 (**2**); 3.22, 1.29 (**3**); 3.21, 1.29 ppm (**4**), respectively. The resonances are interpreted in terms of the triazoles binding to Ag^I atoms in a symmetric fashion in CD_3CN solution.

The ESI-MS spectrum of **1** in CH_3CN/MeOH exhibits peaks at *m*/*z* = 275, 316 and 443, with the appropriate isotopic distributions, that correspond to $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)]^+$, $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)(CH_3CN)]^+$ and $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2]^+$, respectively. No disilver species could be observed in this case. On the other hand, complex **2** exhibits peaks at *m*/*z* = 275, 316, 443, 699 and 1123 in its ESI MS spectrum in CH_3CN, which are assigned to $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)]^+$, $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)(CH_3CN)]^+$, $[Ag(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2]^+$, $[Ag_2(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2(CF_3SO_3)]^+$ and $[Ag_3(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_3(CF_3SO_3)_2]^+$, respectively (Figure 4). The presence of trisilver species in the ESI MS spectrum of **2**, together with the fact that there was only one set of proton resonances in its ^{1}H NMR spectrum, implies that the complex of **2** retains the integrity of its triangular nature in CH_3CN solution. Besides the peaks at *m*/*z* = 275, 316 and 443, the tetranuclear complex **3** also exhibits weak peaks at *m*/*z* = 649, 1023, and 1397 in CH_3CN, which could be assigned to $[Ag_2(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2(ClO_4)]^+$, $[Ag_3(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_3(ClO_4)_2]^+$ and $[Ag_4(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_4(ClO_4)_3]^+$. The presence of Ag_4L_4 species instead of the crystallographically characterized Ag_4L_6 in the ESI MS spectrum of **3** indicates that two of the six triazoles are easily dissociated from the Ag_4 cluster under the conditions of MS measurement. This is in agreement with the crystal structure of **3**. However, since only one set of proton resonances is observed in the ^{1}H NMR spectrum of **3**, we therefore propose that the complex **3** is a fluxional molecule. All the triazoles (the weakly bound and tightly bound ones) exchange their positions very quickly in CH_3CN solution at room temperature.

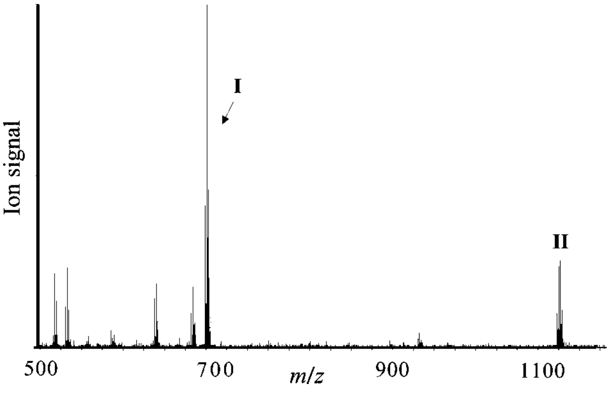


Figure 4. Electrospray mass spectrum of complex **2** in MeCN/MeOH. The ion signals displayed correspond to $[Ag_2(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2(CF_3SO_3)]^+$ (**I**) at *m*/*z* = 699, and $[Ag_3(4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_3(CF_3SO_3)_2]^+$ (**II**) at *m*/*z* = 1123.

Conclusion

In this paper, we describe an interesting case of anion-dependent structural diversity. We found the reaction of Ag^I salts with 4-amino-3,5-diisopropyl-1,2,4-triazole produce complexes of different nuclearity, dependent on the anions employed. The role of the anions consists of determining the coordination geometry of the Ag-centres, namely the N–Ag–N angles in the $(Ag\text{–}N\text{–}N\text{–})_n$ rings. Furthermore, we also found that 4-amino-3,5-diisopropyl-1,2,4-triazole acts as an *exo*-bidentate N-ligand in a somewhat similar way as pyrazolates, although the former is a neutral species.

Experimental Section

4-Amino-3,5-diisopropyl-1,2,4-triazole was prepared according to literature methods.[10] Other reagents were commercially available and used as received.

The CHN microanalyses were carried out with an ELEMENTAR vario EL elemental analyser. IR spectra (KBr pellets) were recorded with a Niclolet Impact 420 FT-IR spectrometer. ^{1}H NMR spectra were recorded with a Bruker DPX-400 spectrometer (400 MHz). Positive ESI mass spectra were recorded with a Waters Q-Tof micro mass spectrometer.

Syntheses

$[Ag_2(\mu_2\text{-}4\text{-}NH_2\text{-}3,5\text{-}iPr_2\text{-}tz)_2(NO_3)_2(CH_3CN)]$ (1): A solution of $AgNO_3$ (0.1 mmol, 17 mg) in MeCN (2 mL) was mixed with a 2-mL ethanol solution of 4-NH_2-3,5-*i*Pr_2-tz (0.1 mmol, 17 mg). The resulting mixture was allowed to evaporate for one week to yield colourless crystals of **1** (30 mg), suitable for X-ray work. Yield: 42%. IR (KBr): $\tilde{\nu}$ = 3222 (m) (NH_2), 2974 (m) (*i*Pr), 1645 (w), 1518 (w), 1383 (s) (NO_3^-), 1110 (w), 1041 (w) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 1.32 (d, 12 H, Me), 3.28 [m, 2 H, H-C(Me)$_2$] ppm.

Table 1. Crystallographic data for **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Formula	$C_{18}H_{35}Ag_2N_{11}O_6$	$C_{27}H_{48}Ag_3F_9N_{12}O_9S_3$	$C_{48}H_{98}Ag_4Cl_4N_{24}O_{17}$	$C_{48}H_{96}Ag_4B_4F_{16}N_{24}$
Molecular weight	717.31	1275.56	1856.78	1788.21
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	10.0878(9)	11.519(3)	24.305(5)	11.996(2)
b [Å]	11.0001(10)	14.550(3)	24.296(5)	22.899(5)
c [Å]	25.927(2)	14.810(3)	13.153(3)	27.986(6)
α [°]		99.651(12)		
β [°]	93.016(2)	94.281(15)	91.41(3)	93.36(3)
γ [°]		90.706(16)		
V [Å^3]	2873.0(5)	2439.4(9)	7765(3)	7675(3)
Z	4	2	4	4
T [K]	298	298	298	298
$\rho_{calcd.}$ [mg/m^3]	1.658	1.737	1.588	1.548
μ [mm^{-1}]	1.414	1.411	1.205	1.093
Reflections collected	16960	23941	19892	20638
Reflections Unique	6266 (R_{int} = 0.0224)	11031 (R_{int} = 0.0170)	11601 (R_{int} = 0.0421)	12343 (R_{int} = 0.0414)
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0363 $wR2$ = 0.0850	$R1$ = 0.0427 $wR2$ = 0.1230	$R1$ = 0.0507 $wR2$ = 0.1195	$R1$ = 0.0430 $wR2$ = 0.0859
S	1.024	1.087	1.022	0.852
$\Delta\rho_{max}$ [e Å^{-3}]	1.010	0.944	0.708	0.571

$C_{18}H_{35}Ag_2N_{11}O_6$ (717.31): calcd. C 30.21, H 4.90, N 21.54; found C 29.53, H 4.86, N 21.58.

[Ag$_3$(μ$_2$-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_3$](CF$_3$SO$_3$)$_3$ (2): A 2-mL aqueous solution of $AgCF_3SO_3$ (0.1 mmol, 26 mg) was mixed with a 2-mL ethanol solution of 4-NH$_2$-3,5-*i*Pr$_2$-tz (0.1 mmol, 17 mg). The resulting mixture was allowed to evaporate for several days to yield colourless crystals of **2** (76 mg). Yield: 60%. IR (KBr): ṽ = 3233 (m), 3122 (m) (NH_2), 2976 (s), 2935 (w) (*i*Pr), 1625 (w), 1517 (m), 1460 (m), 1251 (s) (CF_3), 1172 (s), 1109 (w), 1045 (s), 653 (s), 579 (w), 522 (m) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 1.32 (d, 12 H, Me), 3.25 [m, 2 H, H-C(Me)$_2$] ppm. $C_{27}H_{48}Ag_3F_9N_{12}O_9S_3$ (1275.56): calcd. C 25.47, H 3.77, N 13.21; found C 25.44, H 3.73, N 13.23.

[Ag$_4$(μ$_2$-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_6$](ClO$_4$)$_4$·H$_2$O (3): This compound was prepared as **2** using $AgClO_4$ instead of $AgCF_3SO_3$. Yield: 55% (based on ligand). IR (KBr): ṽ = 3232 (m), 3121 (m) (NH_2), 2975 (m), 2935 (w) (*i*Pr), 1662 (w), 1517 (m), 1461 (w), 1385 (w), 1145 (s), 1089 (s) (ClO_4^-), 631 (m), 549 (w) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 1.29 (d, 12 H, Me), 3.22 [m, 2 H, H-C(Me)$_2$] ppm. $C_{48}H_{98}Ag_4Cl_4N_{24}O_{17}$ (1856.78): calcd. C 31.14, H 5.30, N 18.16; found C 31.11, H 5.38, N 18.11.

[Ag$_4$(μ$_2$-4-NH$_2$-3,5-*i*Pr$_2$-tz)$_6$](BF$_4$)$_4$ (4): This compound was prepared as **2** using $AgBF_4$ instead of $AgCF_3SO_3$. Yield: 53% (based on ligand). IR (KBr): ṽ = 3235 (m), 3122 (m) (NH_2), 2976 (s), 2935 (w), 1660 (w), 1518 (m), 1462 (m), 1385 (w), 1077 (s) (BF_4^-), 527 (w) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 1.29 (d, 12 H, Me), 3.21 [m, 2 H, H-C(Me)$_2$] ppm. $C_{48}H_{96}Ag_4B_4F_{16}N_{24}$ (1788.21): calcd. C 32.29, H 5.38, N 18.83; found C 32.04, H 5.62, N 18.75.

X-ray Crystallography: Diffraction intensities were collected with a Bruker SMART Apex CCD diffractometer (for **1**), Rikagu RAXIS-RAPID imaging plate diffractometer (for **2**) and a Rikagu RAXIS IV imaging plate diffractometer (for **3** and **4**), with graphite-monochromated Mo-K_α radiation. The data collected by CCD diffractometer were processed by *SAINT*,[12] while those collected by Rikagu diffractometers were corrected by "multi-scan" absorption corrections.[13] The structures were solved by direct methods and refined by least-squares on F^2 using the SHELXL program.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were treated as riding. For complexes **2** and **4**, some of the anions and isopropyl groups have been split into two parts with an occupancy factor of 0.5. The lower completeness and lower redundancy of the data for **3** and **4** are probably caused by (a) the poorer quality of crystals of **3** and **4**; (b) the aged detector of the diffractometer used for collection of the intensities. The crystal data for the complexes reported here are summarised in Table 1.

CCDC-620543 to -620546 (for **1**–**4**) 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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