Anion dependence of Ag(I) reactions with 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz): isolation of the molecular propeller compound $[Ag_2(bptz)_3][AsF_6]_2$

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The new compound $[Ag_2(bptz)_3][AsF_6]_2$, prepared from the reaction of bptz with $Ag[AsF_6]$ in CH_3CN, is stable in solution as well as the solid-state and exhibits an unprecedented propeller arrangement of three bptz ligands spanning two Ag(I) ions with $[AsF_6]^-$ anions located in the folds of the cation.

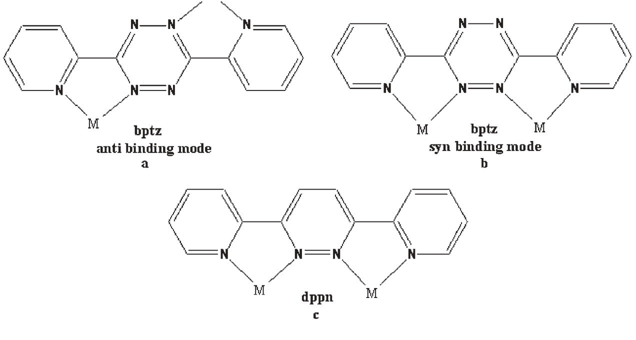
As evidenced by a perusal of the literature, the study of coordination polymers based on silver is a highly active area of supramolecular chemistry.[1] In general, prediction of the structures of self-assembled Ag(I) compounds is difficult because the silver ion is known to adopt a myriad bonding modes and coordination geometries. This situation notwithstanding, considerable progress is being made towards the goal of obtaining specific architectures, for example the recently reported [4 × 5]–Ag_{20} grid,[2a] the Ag_{10} quadruple helicate[2a] and the chiral Ag(I) diamondoid polymer[2a,c] were prepared on the basis of rational design principles. In these cases, carefully chosen multitopic ligands were used whose metal-binding sites direct the self-assembly process to a single outcome.

Clearly, the successful prediction of metal–ligand topologies is central to the issue of controlling inorganic self-assembly reactions, but secondary forces such as hydrogen-bonding, π-stacking, host–guest interactions and ion templation must be considered as well.[3] Of particular relevance to our research is the role of anions in assisting the self-assembly of metal ions, an area that is relatively new as compared to the topic of cation-assisted supramolecular reactions.[4] We have found that reactions of the well-known *N*-heterocyclic ligand 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) are highly dependent on the nature of the anion, as evidenced by the fact that $[Ni(MeCN)_6][BF_4]_2$ reacts with bptz to yield a molecular square[5] whereas the same reaction, performed with the corresponding $[SbF_6]^-$ salt, yields exclusively a molecular pentagon.[6] In both molecular structures, an anion is located inside the cavity of the cationic molecule and appears to be required for the formation of a stable metallocyclophane.

As part of our ongoing interest in bptz chemistry, we noted that Constable *et al.* reported that, unlike the reaction of Cu(I) with the related ligand 3,6-bis(2-pyridyl)pyridazine (dppn) (Scheme 1(c)) which leads to a tetrahedrally-based molecular grid (square), Ag(I) reacts with bptz to yield the one-dimensional polymer $\{[Ag(bptz)_2][BF_4]\}_n$ consisting of Ag(I) atoms bridged by bptz with an *anti*-arrangement of metal ions (Scheme 1(a)),[7a] and the compound $[Ag_2(bptz)_2][CF_3SO_3]_2$ which contains an unusual planar cation in which the bptz ligands are arranged in the less commonly encountered *syn* orientation (Scheme 1(b)).[7b] Given that the products of the $[BF_4]^-$ and $[CF_3SO_3]^-$ salts are so different, we reasoned that the use of other anions would be likely to lead to new derivatives and help to lend insight into the subtle role of anion–cation interactions in dictating the final product.

The reaction of $Ag[AsF_6]$ with bptz in a 2 : 3 ratio in acetonitrile leads to the isolation of dark purple crystals of $[Ag_2(bptz)_3][AsF_6]_2$, (**1**).† A thermal ellipsoid plot of the dinuclear cation $[Ag_2(bptz)_3]^{2+}$ in the asymmetric unit is shown in Fig. 1.[8] The molecular cation consists of two Ag(I) ions coordinated to four nitrogen atoms from three bridging, bptz ligands coordinated in a *syn* fashion. The six-coordinate Ag(I) ions adopt a trigonal prismatic geometry with a propeller-like arrangement of the three bptz moieties. The average Ag–N distance of 2.49[7] Å is in the range of reported values for other bptz complexes of Ag(I);[7] the Ag···Ag separation is 4.2825(10) Å. Also worthy of note is the fact that two F atoms of each $[AsF_6]^-$ anion point towards the centroids of three different tetrazine rings of bptz ligands with relatively short F-ring centroid distances (2.914–3.039 Å) (Fig. 2).

The present result adds to the database of Ag(I) bptz compounds and prompts further contemplation as to why the reaction did not produce a grid as in the case of the Cu(I) reaction with dppn. In the present case, the thermodynamic stability of the compound can be rationalized on the basis that both enthalpic and entropic contributions are favorable (the Ag(I) ions are six-coordinate and the molecule is the smallest possible polynuclear product).[9] As mentioned in the introduction, earlier studies by Constable *et al.*, with the $[CF_3SO_3]^-$ anion also yielded a dinuclear species, namely $[Ag_2(bptz)_2]^{2+}$, but this molecule is much less stable than the new dinuclear cation $[Ag_2(bptz)_3]^{2+}$ reported here as judged by electrospray mass spectral studies which revealed an intense parent ion peak for the intact $[Ag_2(bptz)_3]^{2+}$ cation at a *m*/*z*



Scheme 1 Representation of the (a) *anti* binding mode of bptz, (b) the *syn* binding mode of bptz, and (c) the *syn*-only binding mode of dppn.

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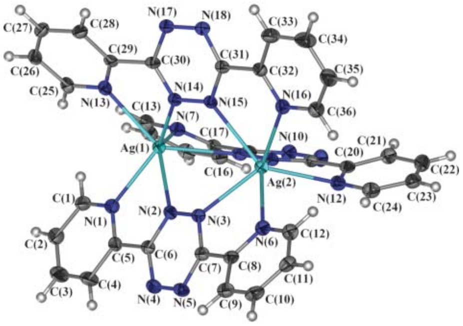

Fig. 1 Thermal ellipsoid plot of the cationic unit $[Ag_2(bptz)_3]^{2+}$ drawn at the 50% probability level.

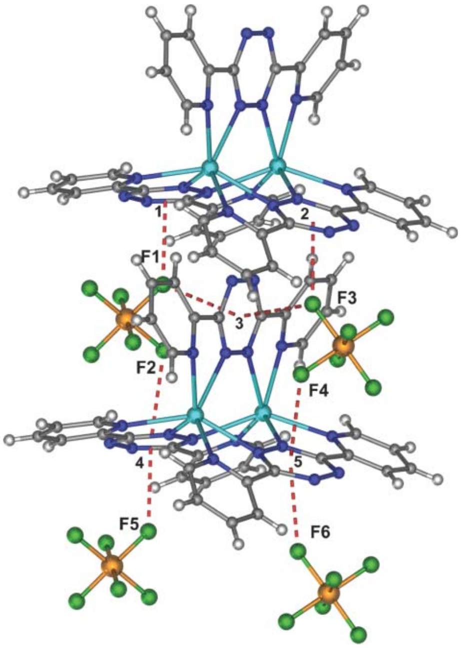

Fig. 2 Representation of the interactions of the cations and anions in $[Ag_2(bptz)_3][AsF_6]_2$. Anion-tetrazine ring contacts: F1–centroid 1 = 2.942 Å, F1–centroid 3 = 2.964 Å, F2–centroid 4 = 3.040 Å, F3–centroid 2 = 2.946 Å, F3–centroid 3 = 2.914 Å, F4–centroid 4 = 2.998 Å, F5–centroid 4 = 2.942 Å, F6–centroid 5 = 3.012 Å.‡

value of 462.9.[10] This result is in contrast to the ESI-MS data for $[Ag_2(bptz)_2][CF_3SO_3]_2$ which support the conclusion that the dominant solution species is the mononuclear fragment $[Ag(bptz)_2]^+$.

In summary, the new compound $[Ag_2(bptz)_3][AsF_6]_2$, (**1**) with an interesting propeller-like molecular structure for the cation, has been characterized in solution as well as the solid-state. These findings lend further support to claims that anions act as templates/controlling elements in the reactions of Ag(I) salts with bptz and related ligands.[1a,7,11] In the present case, the interactions that arise from the packing of the $[AsF_6]^-$ anions in the folds of the cationic propeller molecule appear to be important for stabilizing the structure in the solid-state. The nature of the F-tetrazine contacts *vis-à-vis* anion-π interactions warrants further study by both experimental and computational methods, efforts that are underway in our laboratory.[12]

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Notes and references

† Samples of $AgAsF_6$ (41 mg, 0.14 mmol) and bptz (50 mg, 0.021 mmol) were dissolved in acetonitrile (40 mL) and stirred under nitrogen for 24 hours. The resulting dark purple solution was concentrated to $\sim$10 mL, filtered, and then layered over 20 mL of toluene. Yield of crystals of **1**: 15.5 mg; 16%. A bulk sample was prepared by dissolving quantities of $AgAsF_6$ (41 mg, 0.14 mmol) and bptz (50 mg, 0.021 mmol) in nitromethane. The resulting purple microcrystalline solid was isolated in 78% yield (75.6 mg). An electrospray mass spectrum of the bulk product confirmed the identity as compound **1**: $[Ag_2(bptz)_3]^{2+}$ (m/z = 922.96). Calc. for $[Ag_2(C_{10}H_8N_6)_3][AsF_6]_2$ (%): C, 33.20; H, 1.86; F, 17.5; N, 19.36; found: C, 33.88; H, 2.12; F, 16.91; N, 19.38; O, 2.14. *Crystal data for compound **1***: $C_{40}H_{30}Ag_2As_2F_{12}N_{20}$, $M = 1384.42$, $0.38 \times 0.26 \times 0.19$ mm³, monoclinic, space group $P2_1/c$ (no. 14), $a = 22.879(7)$, $b = 25.283(7)$, $c = 8.125(2)$ Å, $\beta = 90.353(6)°$, $V = 4700(2)$ Å³, $Z = 4$, $D_c = 1.957$ g cm³, $F_{000} = 2712$, Bruker SMART APEX CCD diffractometer, MoKα radiation, $\lambda = 0.71073$ Å, $T = 110(2)$ K, $2\theta_{max} = 55.1°$, 29879 reflections collected, 10007 unique ($R_{int} = 0.0261$). The structure was solved by direct methods in the SHELXL suite of programs with the graphical interface X-Seed. Hydrogen atoms were placed in calculated positions. R factors are based on 8370 reflections with $I > 2\sigma(I)$ (refinement on F^2), 687 parameters. An absorption correction was applied, $\mu = 2.336$ mm^{-1}. GOF = 0.996, $R1 = 0.0342$, $wR2 = 0.0750$.‡

‡ CCDC 229435. See http://www.rsc.org/suppdata/cc/b4/b410811f/ for crystallographic data in .cif or other electronic format.

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