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A robust, porous, cationic silver(I) 3,5-diphenyl-1,2,4-triazolate framework with a uninodal $4^9.6^6$ net†

Guang Yang and Raphael G. Raptis*

Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, PO Box 23346, San Juan, PR 00931, USA. E-mail: Raphael@adam.uprr.pr; Fax: +1-787–7568242; Tel: +1-787–7640000 ext. 2598

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The reactions of silver(I) salts with 3,5-diphenyl-1,2,4-triazole result in three-dimensional, porous, cationic metal–organic frameworks based on novel 6-connected, trigonal-prismatic, pentanuclear silver-triazolate clusters, interconnected by linear N–Ag–N linkers; this robust water- and organic-insoluble structure exhibits both nonpolar-solvent adsorption and anion-exchange properties.

The field of metal–organic hybrid materials with three-dimensional porous structures has experienced spectacular growth in recent years.[1] Both the intellectual challenge of preparing solids with ever increasing porosity, as well as the potential for marketable applications in separations, catalysis, and gas transport, have provided the impetus for those efforts.[2] Advances have depended on the judicious choice of linkers and building units of appropriate coordination algorithms, along with the helpful interventions of serendipity.[3,4] Besides the intensity of the research efforts, only a small number of the mathematically predicted three-dimensional structural motifs have been prepared by chemists to date, due to the fact that several important geometrical motifs have not found chemical counterparts that might serve as building units.[5] The recognition of new molecular building units with geometries of those as-yet-missing motifs will be critical for further progress in this area.

Here we report that a robust, three-dimensional, porous, cationic structure, $\{Ag_3[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6]^{2+}\}_n$, **1**, prepared from AgX and 3,5-Ph_2-tzH,‡ consists of novel trigonal-prismatic $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6^-]$-units connected by further two-coordinate linear Ag-centres—tz = 1,2,4-triazolato anion, X = BF_4^-, NO_3^-, ClO_4^- and CF_3COO^-. The crystal structures of $\{Ag_3[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6](BF_4)_2\cdot 12H_2O\}_n$, $\mathbf{1}(BF_4)_2\cdot 12H_2O$ and $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$ have been determined by single crystal X-ray diffraction studies.§

The reactions of 3,5-Ph_2-tzH with AgX, X = NO_3^-, BF_4^-, ClO_4^- and CF_3COO^-, in a variety of solvents, result in intractable white solids, whose analyses after drying under vacuum are consistent with $\mathbf{1}(X)_2$. The triazole ligands are deprotonated during those reactions, the role of a base being played by H_2O; a hydronium cation surrounded by three H-bonded nitrates is found in one of the two X-ray crystal structures (*vide infra*). Layering an ethanolic solution of the ligand over an aqueous solution of the silver salt results, after slow reagent diffusion, in air-stable single crystals appropriate for X-ray study at the layer interface. Unit cell determinations show that all products are isomorphous, with quite similar cell parameters; complete diffraction data sets were collected only for two crystalline products. X-Ray analyses show both $\mathbf{1}(BF_4)_2\cdot 12H_2O$ and $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$ to be three-dimensional coordination polymers, of $4^9.6^6$ topology, constructed by $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6^-]$-units (Fig. 1) further linked by two-coordinate Ag-centres. The $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6^-]$-units consist of a trigonal-bipyramidal arrangement (inner broken lines, Fig. 1) of the five Ag-atoms, where the axial (located on a 3-fold symmetry axis) and equatorial ones are three- and two-coordinate, respectively. The three equatorial edges of the Ag_5-trigonal bipyramid are not bridged, while the six axial-to-equatorial edges are bridged by triazolate ligands utilizing their N^1- and N^2-atoms. This arrangement leaves the six triazolate N^4-atoms available to coordinate to six further Ag-atoms that radiate from the N^4_6-prism (outer broken lines, Fig. 1) and act as linkers between neighbouring units extending in three dimensions. The six peripheral Ag-atoms, each located on a crystallographic 2_1-axis, define an approximate trigonal-prism of 6.010 Å height and equilateral triangular bases with edges of 10.895 Å. While 6-connected *octahedral* secondary building units (SBU) have been widely utilized in the construction of metal–organic frameworks (MOF),[3] **1** is the first such lattice constructed by 6-connected *prismatic* units. We are aware of only one other example, albeit less regular, of the $4^9.6^6$ topology.[6]

The three-dimensional structure of **1** defines an extended honeycomb lattice (Fig. 2) with hexagonal pores of an approximately 7.8 Å effective diameter running parallel to the crystallographic *c*-axis (a 6_3-axis). Phenyl groups line the pores rendering them hydrophobic. Calculations using the program PLATON show the effective volumes for solvent inclusion to be 1039.0 and 1019.5 $Å^3$ per unit cell, comprising 21.1 and 20.6% of the crystal volume for $\mathbf{1}(BF_4)_2\cdot 12H_2O$ and $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$, respectively.[7] Consistent with the porosity of **1**, adsorption studies monitored by IR spectroscopy indicate that dehydrated samples of **1** readily adsorb nonpolar alkanes, *i.e.* hexane, pentane, cyclohexane†. However, they do not adsorb polar solvents, such as propyl alcohol, ethyl acetate, or thf. The conrotation of the phenyl groups around the pore-axes, along with the unidirectional twisting of the trigonal prismatic $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6^-]$-cluster building units,

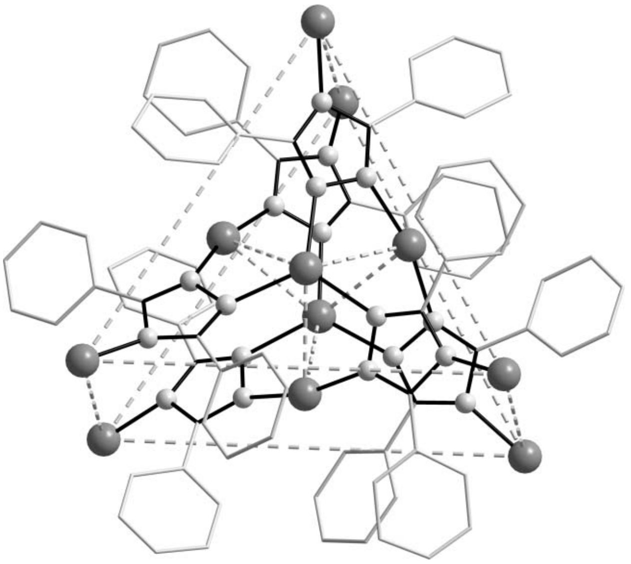

Fig. 1 The trigonal-prismatic $Ag_3[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6]^{2+}$ repeat unit of the three-dimensional structure **1**; Ag—dark grey, N—light grey spheres. Broken lines define the Ag_5-trigonal bipyramid. Selected distances (Å) for $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$ (and $\mathbf{1}(BF_4)_2\cdot 12H_2O$): $Ag_{(ax)}\cdots Ag_{(ax)}$, 3.847(3) (3.627(2)); $Ag_{(eq)}\cdots Ag_{(eq)}$, 4.635(2) (4.764(2)); $Ag_{(eq)}\cdots Ag_{(ax)}$, 3.296(1) (3.295(1)); $Ag_{(ax)}$–N, 2.225(6) (2.235(6)); $Ag_{(eq)}$–N, 2.094(8) (2.118(7)); $Ag_{(peripheral)}$–N, 2.076(6) (2.085(6)).

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† Electronic supplementary information (ESI) available: experimental details, XPRD patterns, TGA curves and IR spectra. See http://www.rsc.org/suppdata/cc/b4/b404269g/

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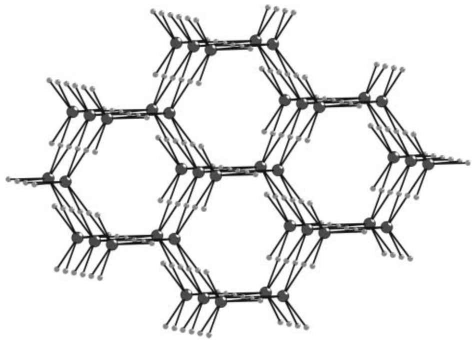

Fig. 2 Schematic view of the $4^9.6^6$ net in the structure of **1**, depicting the hexagonal honeycomb channels parallel to the crystallographic *c*-axis. The centres of $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6{}^-]$-units are denoted by large spheres, which function as 6-connected trigonal prismatic nodes in the net. The small spheres denote the peripheral Ag-atoms, which link two neighbouring $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6{}^-]$-units.

bring about the chirality of the pores. However, even though all pores within any given single crystal are homochiral, the bulk product is a racemic mixture. Furthermore, the unrestricted rotation of all phenyl groups lining the pore surface might cancel the pore chirality when interactions with guest molecules become dominant.

In the X-ray structure of $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$, a hydronium-nitrate dianion, $[(H_3O)(NO_3)_3]^{2-}$, was located from the difference Fourier map, with the hydronium O-atom occupying a site on a crystallographic threefold axis, H-bonded to its three surrounding nitrates. Only one disordered BF_4^- anion was found in Fourier maps of $\mathbf{1}(BF_4)_2\cdot 12H_2O$, with the B-atom also on a threefold axis, but the presence of the required second BF_4-anion is evident from its elemental analysis. Crystallographic disorder over several lattice positions is the obvious reason for the failure to locate this anion as well as the interstitial H_2O molecules required for a good fit of the elemental analysis, TGA and IR data. In both cases, the anions are found confined within the stacks of $[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6{}^-]$-structure, not in the hydrophobic pores.

Thermogravimetric analysis of $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$ shows a weight loss of 7.05% before 100 °C. No further weight loss is observed until the onset of decomposition at 280 °C. Upon drying (*in vacuo*, 100 °C, 1 hour), elemental analysis indicates that besides water, a sample of $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$ also loses one HNO_3 molecule. The framework remains intact during the desorption processes, as indicated by comparison of PXRD of desolvated solids of **1** and that of as-prepared bulk product. A qualitative anion-exchange experiment, monitored by IR spectroscopy, shows that NO_3^- anions can be reversibly exchanged by ClO_4^-, while the framework of **1** undergoes minor structural modification (as determined by PXRD patterns) and remains invariable upon further anion-exchange processes.

A variety of coordination modes have been identified in the transition-metal chemistry of 1,2,4-triazoles (Htz) and triazolates (tz), attracting considerable attention in recent years.[8] The deprotonation of triazoles upon coordination to metal ions in the absence of strong bases, reported here, has also been observed by others.[9] The first silver 1,2,4-triazolate was reported in 1927,[10] while a dinuclear silver-triazole and a two-dimensional silver poly(triazolyl)hydroborate have been structurally characterized more recently.[11,12] The structure of a one-dimensional polymer composed of a macrocyclic ligand containing a triazolate moiety, which bridges three Ag-atoms in a μ_3-*N,N′,N″*-triazolate fashion, is also known.[13]

In summary, reactions of Ag-salts and 3,5-Ph_2-1,2,4-tzH result in a three-dimensional porous MOF featuring the novel 6-connected, trigonal-prismatic Ag_5tz_6-SBU. This framework exhibits both nonpolar solvent adsorption and anion-exchange properties. The isolation of bulk homochiral samples of **1** and related materials remains a challenge, as has been recently pointed out by others as well.[14]

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Notes and references

‡ An ethanol solution (2 ml) of 3,5-di-phenyl-1,2,4-triazole (3,5-Ph_2-tzH) (0.2 mmol, 44 mg) is layered upon an aqueous solution (2 ml) of $AgNO_3$ (0.2 mmol, 34 mg) or $AgBF_4$ (0.2 mmol, 38 mg). Colourless needles are formed at the interface within one month in 69% or 52% yield for nitrate and tetrafluoroborate salts respectively. $\{Ag_3[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6](H_3O)(NO_3)_3\cdot 9H_2O\}_n$ Anal. Calcd. for $C_{84}H_{63}Ag_8N_{21}O_{10}\cdot 9H_2O$: C, 39.5; H, 3.2; N, 11.5 Found: C, 39.5; H, 2.9; N, 11.3%. $\{Ag_3[Ag_5(\mu_3\text{-}3,5\text{-}Ph_2\text{-}tz)_6](BF_4)_2\cdot 12H_2O\}_n$ Anal. Calcd. for $C_{84}H_{60}Ag_8B_2F_8N_{18}\cdot 12H_2O$: C, 39.2; H, 3.3; N, 9.8; F, 5.9 Found C, 39.7; H, 3.5; N, 9.9; F, 6.1%.

§ Crystal data (Siemens SMART 1K CCD diffractometer, Mo-Kα radiation, 293 K): for $\mathbf{1}(H_3O)(NO_3)_3\cdot 9H_2O$, $C_{84}H_{63}Ag_8N_{21}O_{10}$, $M = 2389.51$, hexagonal, $P6_322$ (No. 182), $a = b = 21.790(3)$, $c = 12.020(2)$ Å, $V = 4942.5(14)$ Å^3, $Z = 2$, $\rho_{\text{calcd.}} = 1.604$ g cm^{-3}, $\mu = 1.611$ mm^{-1}, 29229 reflections collected, 3805 independent ($R_{\text{int}} = 0.1382$), 154 parameters, 5 restraints, $R_1 = 0.0655$ for 1806 observed reflections with $I > 2\sigma(I)$ (0.1616 for all data), $wR_2 = 0.1626$, $S = 0.923$, max. $\Delta\rho = 1.571$ e Å^{-3}. For $\mathbf{1}(BF_4)_2\cdot 12H_2O$, $C_{84}H_{60}Ag_8B_2F_8N_{18}$, $M = 2358.08$, hexagonal, $P6_322$ (No. 182), $a = b = 21.599(3)$, $c = 12.196(2)$ Å, $V = 4927.3(14)$ Å^3, $Z = 2$, $\rho_{\text{calcd.}} = 1.589$ g cm^{-3}, $\mu = 1.618$ mm^{-1}, 29339 reflections collected, 3950 independent ($R_{\text{int}} = 0.0754$), 178 parameters, no restraints, $R_1 = 0.0533$ for 2365 observed reflections with $I > 2\sigma(I)$ (0.1076 for all data), $wR_2 = 0.1580$, $S = 1.016$, max. $\Delta\rho = 1.400$ e Å^{-3}. CCDC 234366 and 234367. See http://www.rsc.org/suppdata/cc/b4/b404269g/ for crystallographic data in .cif or other electronic format.

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