Simple routes to supramolecular squares with ligand corners: 1 : 1 Ag^I : pyrimidine cationic tetranuclear assemblies

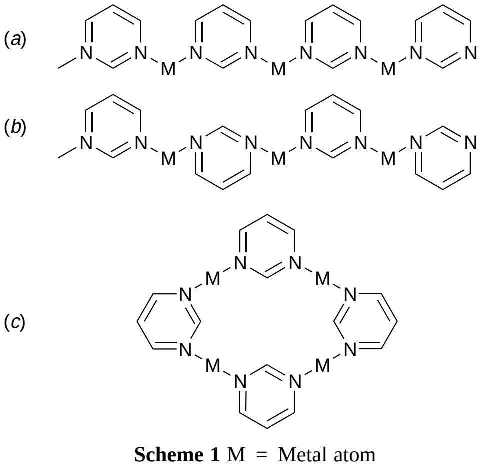
C. V. Krishnamohan Sharma, Scott T. Griffin and Robin D. Rogers*

Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

Simple, tetranuclear cationic supramolecular squares with ligands at the corners can be constructed using the geometry of the pyrimidine ligand and the directional tendencies of Ag^I coordination; the 1 : 1 Ag^I : pyrimidine squares have an open channel structure which facilitates selective ion exchange of pertechnetate over nitrate.

Discrete macrocyclic metal complexes and coordination polymers with open networks constitute a new family of inorganic host materials.[1,2] While inorganic macrocycles with their conformational rigidity provide an alternative to organic macrocycles such as, crown ethers, cyclophanes, and calixarenes, the open network coordination polymers represent zeolite-like materials with fine-tunable cavities and/or ion exchange properties.[1–3] The robustness of inorganic frameworks and their ability to selectively bind anionic species make them particularly suitable to extract a variety of anions.[3] Here, we report crystal engineering strategies for synthesizing novel supramolecular squares through tetranuclear self-assembly of Ag^I cations and pyrimidine ligands.[1] These supramolecular squares may be used to selectively remove the radioactive TcO_4^- anion from solution, currently a technological challenge in the clean-up of the Hanford radioactive waste tanks in the US.[4]

In general, formation of cyclamers, oligomers, or polymers in transition metal complexes depends on the coordination geometry of the metal, the metal to ligand ratio, the chemical structure of the organic ligands, and the donicity of counterion.[2,5] The 1 : 1 transition metal complexes of linear bifunctional ligands such as pyrazine and 4,4′-bipyridyl are known to form one-dimensional coordination polymers, but the possible network topologies for analogous metal complexes with simple angular bifunctional ligands, *e.g.* pyrimidine, are not well studied.[3,5b,6][†] However, one can reasonably anticipate three different networks, or supramolecular isomers, for 1 : 1 pyrimidine metal complexes as delineated in Scheme 1.[7] Indeed, one type of isomer, discrete supramolecular squares [Scheme 1(*c*)], is of current interest owing to their potential host properties. Current synthetic strategies focus on using metal ions at the corners and linear ligands as the spacers, which often requires occupying several of the metal's coordination sites with chelating ligands to force discrete macrocycle formation.[1] We undertook the inverse, construction of such squares utilizing a ligand with angular geometry (pyrimidine) at the corners and a metal with a tendency for linear coordination (Ag^I) as the spacer.



Scheme 1 M = Metal atom

Crystals of [Ag(pyrimidine)][NO_3] **1**, were obtained when methanolic solution (15 ml) of pyrimidine (0.08 g, 1 mmol) was reacted with $AgNO_3$ (0.169 g, 1 mmol) dissolved in acetonitrile (15 ml) through careful layering in a test tube at room temp. Complex **1** is an interesting cyclic self-assembly of pyrimidine and Ag^I forming a supramolecular square with H···H contacts within the cavity *ca.* 3.8 × 3.8 Å [Scheme 1(*c*), Fig. 1].[‡] The squares exist in planar sheets with each square face-to-face stacked to six other squares (one edged stacked and two corner stacked each, in the sheets above and below the square plane, Fig. 2) at 3.45 Å. The planar sheets coincide every fifth sheet, thus the channels perpendicular to each plane of squares, are actually formed both by open squares and by an edge and two corners of three squares in the planes above and below. The NO_3^- anions are inside the channels and are weakly coordinated with the Ag^I cations (nine Ag···O interactions in the range 2.6–3.2 Å) and accept aromatic C–H···O hydrogen bonds. There are as many as 18 C–H···O hydrogen bonds with C···O

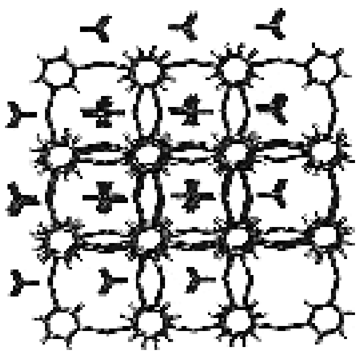


Fig. 1 Packing diagram of **1**. The channels depicted are formed from the supramolecular square in every fifth plane and by an edge and two corners of a total of three squares in all other planes. Additional channels through the centers of the squares exist at an angle to the square plane.

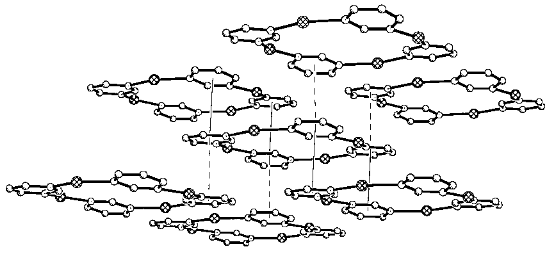


Fig. 2 The face-to-face stacking of a supramolecular square to six other squares is indicated with solid (square edges stacked) and dashed (square corners stacked) lines

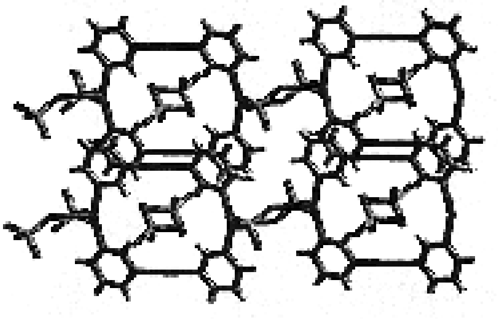


Fig. 3 The 1D coordination polymers of **2** are stacked to form open channel networks

distances and C–H$\cdots$O angles in the range 3.0–3.5 Å and 110.7–150.4°.[8]

Because of the open and hydrophobic nature of the channels and the weak cation and anion interactions, we attempted to exchange the nitrate anions with larger softer anions such as ReO_4^- and TcO_4^-. 0.0158 g of complex **1** crystals were suspended in 1 ml of MeOH containing 0.114 μCi of $NH_4\,^{99}TcO_4$. After stirring for 2 h the activity of the solution was reduced by 12%. A significant reduction in the activity, *ca.* 40%, was observed after 24 h and the distribution ratio for TcO_4^- was calculated to be 95.§ We also examined the radioactivity of the above crystals after washing them thoroughly with fresh MeOH. A 0.008 g sample of the crystalline material used above showed an activity of 885 counts min^{-1} confirming the presence of TcO_4^-. Further, dissolution of complex **1** (0.062 g, 0.25 mmol) in 25 ml of MeOH–H_2O (3 : 1) containing $NaReO_4$ (0.068 g, 0.25 mmol) and recrystallization at room temp., yielded crystals of [Ag(pyrimidine)][ReO_4] **2**. Complex **2** also consists of supramolecular squares (internal cavity H$\cdots$H separations*ca.* 3.3 × 4.3 Å) as observed in **1** with ReO_4^- both in the open channels and forming a 1D coordination polymer [Ag–O, 2.413(8), 2.480(10) Å] as shown in Fig. 3. The ReO_4^- anions in the channels form 15 C–H$\cdots$O hydrogen bonds (C$\cdots$O distances and C–H$\cdots$O angles are within the ranges of 3.1–3.5 Å and 110.0–143.5°, respectively) in addition to long Ag$\cdots$O contacts (four contacts found between 2.8 and 3.0 Å). The 3D structure of **2** is stabilized by face-to-face stacking of square edges (3.44 Å) such that each square stacks with only two other squares in a stair-step fashion (one above and one below the square plane, Fig. 3).

Our attempts to grow single crystals of the 1 : 1 complex of $AgClO_4$ (0.207 g, 1 mmol) and pyrimidine (0.08 g, 1 mmol) from MeOH (25 ml, room temp.) resulted in an unexpected 5 : 6 complex, $[Ag_{2.5}(pyrimidine)_3][ClO_4]_{2.5}$ **3**. The crystal structure of **3** is a 1D coordination polymer with supramolecular squares similar to **1** and **2** (internal cavity H$\cdots$H separation,*ca.* 2.8 × 4.8 Å) but the squares are crosslinked by a dimeric pyrimidine unit vertically in a staircase fashion as shown in Fig. 4. Indeed, this is a combination of possible isomers outlined for 1 : 1 metal complexes in Scheme 1. One of the ClO_4^- anions is coordinated to Ag [Ag–O 2.496(7) Å] and one is found to be disordered. Further, the anions have eight Ag$\cdots$O contacts between 2.7 and 3.2 Å and 20 C–H$\cdots$O hydrogen bonds (C$\cdots$O distances and C–H$\cdots$O angles are within the ranges 3.1–3.5 Å and 113.0–172.5°, respectively). The 1D layers of **3** are face-to-face stacked on square edges in a stair-step fashion as observed for **2**, but at a longer 3.87 Å separation.

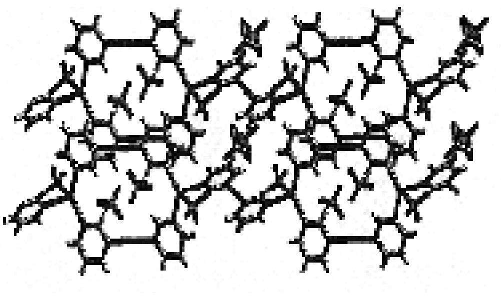


Fig. 4 The supramolecular squares of **3** are vertically crosslinked by dipyrimidine units in a staircase fashion to form 1D coordination polymers. The polymers are face-to-face stacked on edge in a stair-step fashion as observed in **2** albeit at a longer aromatic$\cdots$aromatic separation. Note that one of the ClO_4^- anions is disordered.

In conclusion, the angular geometry of pyrimidine or of any other simple angular bifunctional ligands may be readily exploited to construct discrete inorganic macrocyclics and a variety of coordination polymers as well, by making subtle changes in the metal/ligand ratio (including the uncommon ratios as observed for complex **3**) or donicity of the anion. Currently, we are investigating the conditions required for preferential formation of the descrete supramolecular square *vs.* the 1D/2D coordination polymers in complexes of pyrimidine and its derivatives.

Footnotes and References

* E-mail: RDRogers@UA1VM.ua.edu

† A survey of the Cambridge Structural Database (April, 1997 release) for simple pyrimidine metal complexes resulted in five hits. Of these, only two complexes contain pyrimidine exclusively as a ligand, *i.e.*, with no other ligands additionally bonded to the metal (Refcodes: PMDPTA, PMDPTB). However, recently, pyrimidine has been used to generate an acentric 3D coordination polymer of Cu^I, S. W. Keller, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 247.

‡ *Crystal data*: **1** [Ag(pyrimidine)][NO_3], M = 249.97, triclinic, space group $P\bar{1}$, a = 7.3996(3), b = 9.4356(3), c = 10.3679(4) Å, α = 90.046(1), β = 71.437(1), γ = 74.406(1)°, U = 658.00(4) Å^3, Z = 4, D_c = 2.523 Mg m^{-3}, $F(000)$ = 480. R = 0.086, R_w = 0.215.

2: [Ag(pyrimidine)][ReO_4], M = 483.16, triclinic, $P\bar{1}$, a = 7.895(2), b = 8.095(3), c = 12.643(3) Å, α = 91.95(2), β = 96.11(1), γ = 98.51(1)°, U = 793.5(4) Å^3, Z = 4, D_c = 3.668 Mg m^{-3}, $F(000)$ = 784. 3081 absorption corrected reflections out of 3611 unique reflections measured at 173 K for a crystal of dimensions, 0.04 × 0.10 × 0.18 mm, on convergence gave final values of R = 0.039, R_w = 0.090.

3: $[Ag_{2.5}(pyrimidine)_3][ClO_4]_{2.5}$, M = 758.58, triclinic, $P\bar{1}$, a = 7.2417(3), b = 8.1714(8), c = 19.187(2) Å, α = 81.274(2), β = 80.608(2), γ = 75.215(2)°, U = 1075.8(2) Å^3, Z = 2, D_c = 2.342 Mg m^{-3}, $F(000)$ = 732. 2673 absorption corrected reflections out of 3171 unique reflections measured at 173 K for a crystal of dimensions, 0.20 × 0.30 × 0.38 mm, on convergence gave final values of R = 0.050, R_w = 0.111.

Data on **1**, **2** and **3** were collected with a Siemens CCD area detector (4 $< \theta <$ 56°). All non-H atoms were anisotropically refined and aromatic H atoms were calculated (d_{C-H} = 0.95 Å) and fixed with the thermal parameters based upon the C atom to which they are bonded. CCDC 182/695.

§ The distribution ratio was calculated from $[(A_i - A_f/A_f)$(volume of MeOH in ml/mass of complex **1** crystals, g)], where A_i = initial ^{99}Tc activity, A_f = final ^{99}Tc activity in the solution.

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