Synthesis and structure of a platinum(II) molecular square incorporating four fluxional thiacrown ligands: The crystal structure of $[Pt_4([9]aneS_3)_4(4,4'\text{-bipy})_4](OTf)_8$†

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A Pt(II) molecular square containing four fluxional trithiacrown ligands at the corners is prepared by transition metal-mediated self-assembly.

During the past decade, molecular squares based upon metal–organic frameworks and formed by transition metal-mediated self-assembly have emerged as a key component in the field of supramolecular chemistry.[1,2] Supramolecular 2-D and 3-D metal–organic networks can form porous solids, which can be engineered with specific applications in fields such as artificial molecular machines, hydrogen storage, heterogeneous catalysis and host–guest interactions.[3] Using Pt(II) and Pd(II) corners to direct *cis* self-assembly with bridging diimines such as 4,4′-bipy (4,4′-bipyridine) and related ligands, Stang and Fujita have pioneered the development of molecular squares built upon metal–organic frameworks.[4,5] Adjacent *cis* sites on the exterior of a metal corner are typically blocked using diphosphine (non-aqueous solvent) or diamine (aqueous solvent) ligands, and the self-assembly to the square is directed by the metal corner.[6,7]

Our group is interested in extending this supramolecular chemistry to include thiacrowns, such as $[9]aneS_3$ (1,4,7-trithiacyclononane), as alternative capping ligands. Surprisingly, little work in the field has been undertaken with these interesting macrocycles, although a molecular cube formed by transition metal-mediated self-assembly and containing Ru(II)/$[9]aneS_3$ corners has been reported.[8] The Pt(II) and Pd(II) coordination chemistry of these thiacrowns shows remarkable physico-chemical properties, including readily accessible trivalent oxidation states and unusual spectroscopic behavior, which could then be incorporated into the square.[9,10] We are especially interested in the dynamic behavior of the thioether ligands on the four corners of the molecular square, since ligand fluxionality is not commonly seen in these types of rigid metal–organic frameworks.[1,2]

Here we report the synthesis and characterization of a molecular square **1** with capping $[9]aneS_3$ ligands, formed *via* self-assembly mediated by Pt(II). The four corners of **1** are comprised of Pt(II) ions, each one coordinated by one $[9]aneS_3$ ligand and bridged by four diimine ligands 4,4′-bipyridine (4,4′-bipy). All four corners of **1** show the axial Pt–S interactions that account for the unusual Pt(II) coordination chemistry of $[9]aneS_3$.[11] As expected, each one of the four $[9]aneS_3$ ligands is fluxional on the rigid Pt(II) square metal–organic framework, "turning like four wheels on a wagon".

Dechlorination of the starting complex $[Pt([9]aneS_3)Cl_2]$ using silver triflate is the initial step in the formation of **1** (see ESI†). Subsequent reaction with 4,4′-bipy in CH_3CN over several days forms **1** in good yield. We also note that **1** forms readily, even in the presence of excess ligand, as we have not been able to isolate a corner fragment (2 bipy/1 Pt moiety) with reaction stoichiometries containing a large excess of 4,4′-bipy.[12] The combustion analysis of the product is consistent with the formation of **1**, which is further supported by multi-nuclear NMR and other data (see ESI†). The symmetrical bridging of each 4,4′-bipy ligand to the Pt(II) corners is confirmed by its simple ^1H and ^{13}C NMR spectra. A single Pt resonance in the ^{195}Pt NMR spectrum shows the equivalency of all four Pt(II) corners. Moreover, the ^{195}Pt NMR chemical shift at −3134 ppm is consistent with a S_2N_2(diimine) + S_1 coordination environment.[13] The fluxional nature of the four $9[ane]S_3$ ligands is clearly demonstrated, since only a single ^{13}C NMR resonance is observed for all 24 methylene carbons. Although **1** is constructed through a rigid metal–organic framework, we note that over half of the atoms in the cation of **1** are in a state of flux.

Formation of **1** is verified conclusively *via* its X-ray structure,[14] and an ORTEP drawing of the complex cation is shown in Fig. 1. The structure consists of an 8+ molecular square cation, with four 4,4′-bipy ligands bridging between four corners composed of Pt/$[9]aneS_3$ moieties (charge balance provided by triflate anions). The asymmetric unit was chosen to contain two Pt $[9]aneS_3$ moieties and two complete 4,4′-bipy linkers. The complete $[Pt_4([9]aneS_3)_4(4,4'\text{-bipy})_4]^{8+}$ complex cation lies about a two-fold axis. The coordination environment at each Pt(II) center is best described as $S_2N_2 + S_1$, and consists of an elongated square pyramid formed by one $[9]aneS_3$ and two mutually *cis*-coordinated bridging bidentate 4,4′-bipy ligands. The presence of two Pt–S equatorial bonds (Pt1–S2 2.259(3) Å, Pt1–S3 2.261(3) Å, Pt2–S5 2.241(3) Å and Pt2–S6 2.248(3) Å) along with one longer Pt–S axial interaction (Pt1–S1 3.0344(35) Å and Pt2–S4 3.1214(30) Å), common in Pd(II) and Pt(II) $[9]aneS_3$ coordination chemistry, is also observed here at each Pt center.[8,13] At opposite corners of the square, the axial Pt–S interactions point in the same direction (two up and two down). The N–Pt–N angles (N1–Pt1–N2 89.9(4)° and N3–Pt2–N4 87.9(4)°) display nearly perpendicular *cis*-coordination sites at each Pt center. The square is buckled however, with each Pt displaced by 0.68 Å from the least-squares plane calculated from

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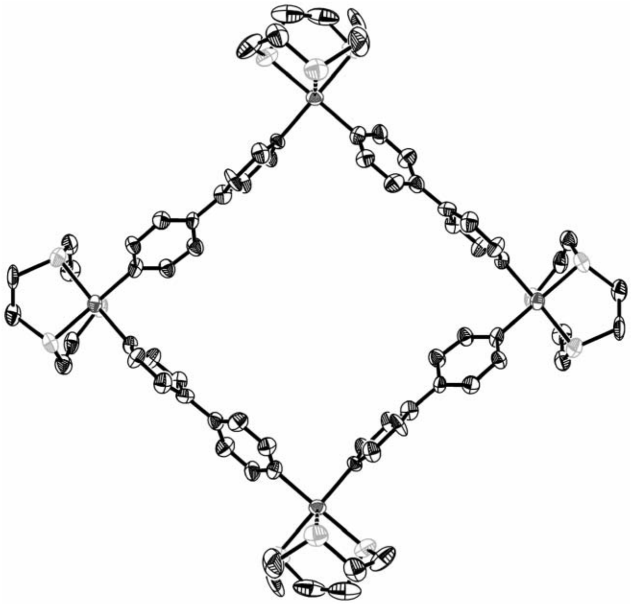

Fig. 1 ORTEP diagram of $\mathbf{1}^{8+}$ (ellipsoids drawn at 50% probability).

the 4 corner positions of the square. The 4,4′-bipy linkers also exhibit a typical twist angle between the two pyridine rings (32.6 and 34.9°).[6,7]

Disordered nitromethane solvate molecules, found during structural refinement, were removed using the program SQUEEZE.[15] The presence of nitromethane solvate molecules in the crystal was consistent with the bulk elemental analysis data and crystal growth conditions. The SQUEEZE program located four solvent-accessible voids in the structure, each with enough volume for two nitromethane and four water solvate molecules per $[Pt([9]aneS_3)(bipy)]_4(OTf)_8$ unit, consistent with the bulk chemical analysis (see ESI†). Interestingly, what would have been the cation "cavities" in the crystal are filled with four triflate anions. The solvent voids are *not* located there but rather lie in regions between the cation squares.

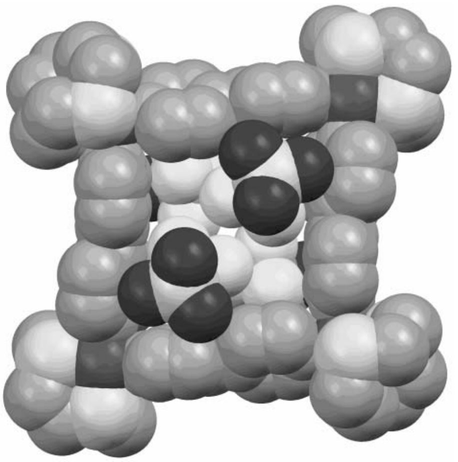

Fig. 2 Space-filling diagram of **1** showing the location of triflate anions within the square cavity; the darkest spheres are oxygens and the lightest spheres are fluorines.

Each one of the square cavities is occupied by four triflate anions as shown in Fig. 2. Many short F–F interactions dominate the triflate arrangement as the CF_3 groups all point into the square holes, while all of the anionic SO_3^- groups of the triflates point away from the holes. The fluorous regions of the triflate CF_3 groups inside the square are confined to within a relatively non-polar hydrocarbon-lined cavity formed by the bipy linkers. We believe that the triflate anions may play an important role in the self-assembly of this square structure as our efforts to date to synthesize this 8+ cation with other anions, such as PF_6^-, have not yielded molecular squares, even after extended reaction times. Of the only two other structurally characterized molecular squares of Pt(II) containing 4,4′-bipy bridges, the square cavities are either occupied by cations or the occupancy is unclear. Therefore, this new family of thiacrown molecular squares may find applications in anion binding and recognition.[6,7] The remaining four triflates per formula unit are found in regions between squares. Additionally, the molecular square cations all pack parallel in an ABAB layered structure along the crystallographic b-axis. Fig. 3 shows the two unique packing layer positions of squares, and the location of triflate anions within and between the square cavities.

In conclusion, we have used transition metal-mediated self-assembly to prepare a Pt(II) molecular square that incorporates a dynamic, fluxional trithiacrown ligand into a rigid metal–organic framework. Half of the triflate anions fill the square cavities *via* association through F–F interactions. Efforts are under way to extend this chemistry to other d^8 metal ions and bridging organic molecules.

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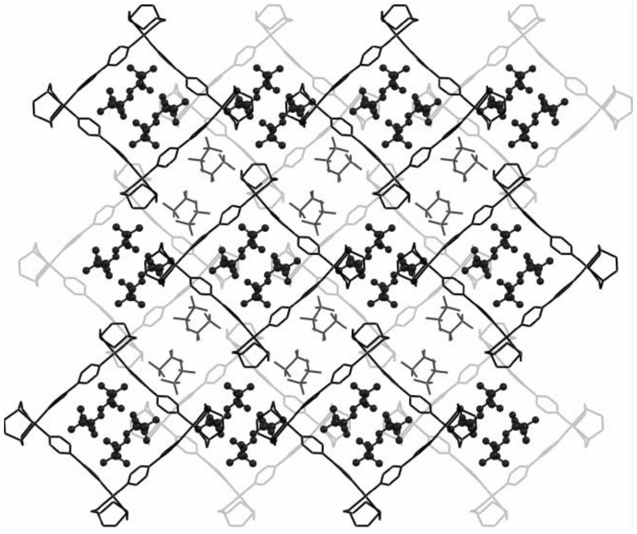

Fig. 3 Packing diagram of **1** viewed parallel to the b-axis. Black indicates squares in the same layer, gray indicates squares in another layer. Triflates inside squares are shown as ball-and-stick models, triflates between squares are shown as wire-frame models.

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14 Crystal data for **1**: $C_{72}H_{80}F_{24}N_8O_{24}Pt_4S_{20}$, $M = 3319.00$, $T = 183(2)$ K, monoclinic, $C2/c$, $a = 33.022(7)$, $b = 13.987(3)$, $c = 26.107(5)$ Å, $\beta = 95.24(3)^\circ$, $V = 12008(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 5.093 mm^{-1}, 40509 reflections collected, 10663 unique ($R_{int} = 0.0852$), data/restraints/parameters = 10663/0/692, $R1 = 0.0780$ for $I > 2\sigma(I)$, w$R2$ (all data) = 0.2099. CCDC 609042. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606753k.

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