ARTICLE

Co-crystals of tetrahaloauric acid and 1,3,5-(methylacetamide)benzene-based tectons: consistent trapping of high energy molecular conformation†

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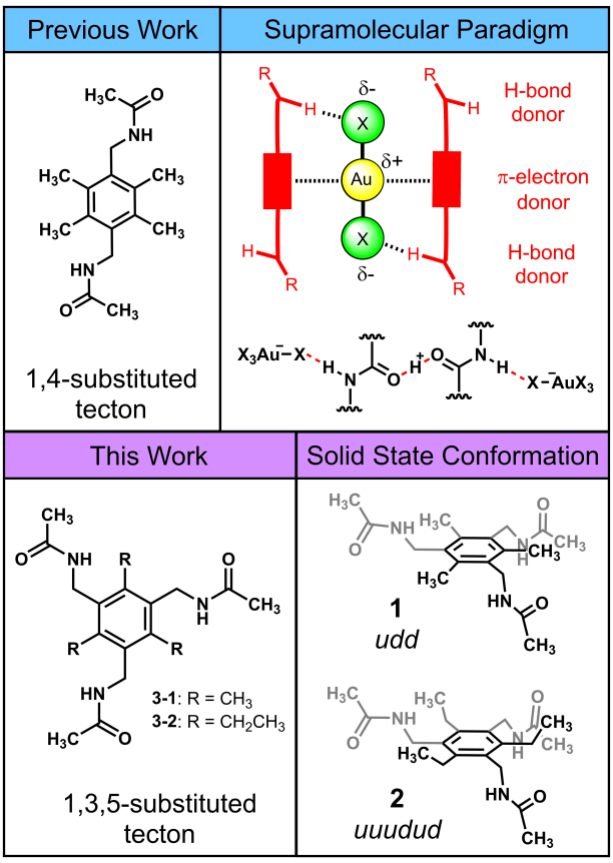
Co-crystal engineering is a promising method to create new classes of advanced materials. Co-crystal structure prediction is more challenging when one or more of the lattice constituents (tectons) are flexible molecules. This study reports four co-crystals that were prepared by mixing $HAuCl_4$ or $HAuBr_4$ with C3-symmetric tectons based on a 1,3,5-(methylacetamide)benzene scaffold. X-ray analysis of the co-crystals revealed the presence of three dominant supramolecular interactions; (a) hydrogen bonding between tecton amide NH residues and the AuX_4^- anion, (b) electrostatic stacking of the Au center against the tecton's π-electrons, (c) very short hydrogen bonds within a proton-bridged-carbonyls motif. Within all four co-crystals, the sterically-geared tecton was trapped in a high energy molecular conformation, which increased the number of favorable intermolecular interactions in the lattice. We infer from the results that the likelihood of high energy molecular conformations within a co-crystal increases if there are multiple dominant intermolecular interactions. Application of this generalizable rule should lead to improved crystal structure prediction.

Introduction

Co-crystal engineering is attracting increased interest as a promising way to produce new materials with interesting properties, and ongoing research is developing reliable design rules for co-crystallization.[1 2 3 4] The size and shape of the constituent molecules (referred to here as tectons)[5] are important factors that control the lattice arrangements, along with the strength and directionality of the close intermolecular interactions generated by the solid-state packing.[6 7] In principle, it is relatively easy to predict the likely co-crystal lattice packing when all the tectons are rigid molecules with well-defined shapes. Co-crystal lattice prediction becomes more challenging if some or all of the tectons are flexible molecules.[6 7 8] In this case, the simplest conceptual approach is to assume that all the flexible tectons adopt their lowest energy conformation. However, this paradigm ignores the possibility that a flexible tecton in a high-energy conformation might permit more favorable solid-state packing due to improved positioning of the functional groups. In other words, an increased number of favorable intermolecular interactions can offset the energetic penalty that is incurred when a tecton adopts a high energy molecular conformation.[6 9]

While there are literature reports of co-crystals that fortuitously trap a molecule in a high energy conformation,[10] there are few examples of a co-crystallization platform that does so in a reliable fashion. One interesting example is Kemp's triacid (cis,cis-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) which can adopt two



Scheme 1. (Top) Previous co-crystallization work using 1,4-substituted tectons. (Bottom) The 1,3,5-substituted tectons used in this study and the high energy conformers observed in the co-crystal structures.

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Table 1. Selected crystal structure and refinement data.

	1·$HAuCl_4$	**1**·$HAuBr_4$	**2**·$HAuCl_4$	**2**·$HAuBr_4$
Empirical formula	$C_{18}H_{28}AuCl_4N_3O_3$	$C_{76}H_{122}Au_4Br_{16}N_{12}O_{13}$	$C_{21}H_{34}AuCl_4N_3O_3$	$C_{21}H_{34}AuBr_4N_3O_3$
Formula weight	673.20	3478.27	715.28	893.12
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	$P2_1/n$	$P2_1/n$
Volume	1193.03(14) Å^3	2935.2(15) Å^3	2675.7(3) Å^3	2791.3(4) Å^3
Final R indices [I>2σ(I)]	R_1 = 0.0320, wR_2 = 0.0525	R_1 = 0.0837, wR_2 = 0.2106	R_1 = 0.0167, wR_2 = 0.0346	R_1 = 0.0211, wR_2 = 0.0438
R indices (all data)	R_1 = 0.0488, wR_2 = 0.0561	R_1 = 0.1279, wR_2 = 0.2383	R_1 = 0.0269, wR_2 = 0.0380	R_1 = 0.0373, wR_2 = 0.0485

different cyclohexane chair conformations of unequal energy.[11] In its tricarboxylate form, the molecule favors the cyclohexane chair conformation with all carboxylates in an equatorial position, which reduces electrostatic repulsions between the anionic carboxylates. But co-crystallization of Kemp's triacid with tectons that provide a proton, or act as a counter cation, induces a switch to the alternative cyclohexane chair conformation with some or all of the carboxylates in an axial position.[12 13 14 15 16 17] In these salt co- crystallization cases, the energetic landscape is relatively easy to rationalize since the lattice packing of ionic tectons is dominated by electrostatics. Here, we address a more subtle co-crystallization circumstance; consistent co-crystal packing of a neutral tecton in its high energy conformation.[10] The absence of charged atoms means the packing energy landscape is relatively flat, which makes it much harder to predict the co-crystallization outcome.

The neutral tectons in this report belong to a well-known family of aryl derivatives with a sterically-geared arrangement of substituents around the molecular periphery.[18 19 20] The two homologous compounds **1** and **2** (shown in the bottom of Scheme 1) have three methylacetamide substituents on a central aryl ring in a 1,3,5-orientation. The lowest energy conformation of these C3-symmetric compounds locates the adjacent substituents in spatial positions that avoid steric clashes. In the case of **1**, all three methylacetamide substituents are directed "down" relative to the plane of the central aryl ring and the lowest energy conformation is called *ddd* where *d* = down.[18] In the case of **2**, the orientation of each ethyl substituent on the aryl ring also has to be defined, and therefore the lowest energy conformation is called *dududu* where *u* = up. The molecular pre-organization induced by this sterically-geared scaffold is the basis of many supramolecular receptors for non-covalent recognition of various guests in solution.[21 22 23 24] Many of these complexes have been characterized by single crystal X-ray diffraction and while the majority of co-crystal structures include the sterically-geared scaffold in the expected lowest energy conformation, there are also examples where the scaffold adopts a higher energy conformation.[25 26 27 28 29 30 31 32 33 34] To the best of our knowledge, there is no co-crystallization platform that consistently traps the sterically-geared scaffold in a high energy molecular conformation.

Recently, we reported a set of co-crystallization studies that mixed $HAuCl_4$ or $HAuBr_4$ with C2-symmetric tectons like 1,4-bis(methylacetamide)-2,3,5,6-tetramethylbenzene (see the top of Scheme 1).[35] X-ray analysis of the co-crystals revealed three consistent supramolecular interactions in all structures; (a) hydrogen bonding between amide NH residues of the tecton and the electronegative X ligands on the AuX_4^- anion (NH···X interaction), (b) electrostatic stacking of an electron deficient Au center against the tecton's aromatic surface (Au···π interaction), (c) very short hydrogen bonds within a proton-bridged-carbonyls motif (CO···H^+···OC) that creates a linear polymer chain of linked tectons. We were curious if, and how, these three primary non-covalent interactions would be maintained if we used a less symmetric tecton that possessed the requisite functional groups to form all non-covalent bonds. Here, we describe the results of four co-crystallization experiments that mixed $HAuCl_4$ or $HAuBr_4$ with tectons **1** or **2** to produce co-precipitates that were amenable to recrystallization. X-ray diffraction analysis of the co-crystals revealed that all three non-covalent interactions were present in each solid-state structure, and the C3-symmetric tecton was forced to adopt a high energy conformation. The results include a trend that can be exploited for crystal structure prediction.

Experimental

General Materials and Methods

Materials. All chemicals and solvents were purchased as reagent grade and used without further purification unless otherwise noted. Chloroauric acid was purchased from Oakwood Chemical while bromoauric acid was purchased from Strem Chemicals. Reactions were monitored by analytical thin-layer chromatography (TLC) on silica gel 60-F254 plates, visualized by ultraviolet (254, 365 nm). NMR spectra (^{1}H, ^{13}C) were recorded on Bruker AVANCE III HD 400 or 500 MHz spectrometer at 25 °C. Chemical shift was presented in ppm and referenced by residual solvent peak. High-resolution mass spectrometry (HRMS) was performed using a Bruker micro TOF II spectrometer.

Synthesis. The organic tectons **1** and **2** were readily synthesized by following previously published procedures that are described in the Electronic Supplementary Information.[36–38] The co-precipitation experiments mixed tectons **1** or **2** (4 mM) in $CHCl_3$ (0.3 mL) with an equal volume of $HAuCl_4$ or $HAuBr_4$ (4 mM) in dibutyl carbitol and the solution became cloudy almost immediately. Each sample was centrifuged (4500 rpm, 5 min) and the gold pellet collected for recrystallization. Single crystals suitable for X-ray diffraction were obtained by using the specific crystallization conditions described in the Electronic Supplementary Information.

Crystallography

Data was acquired using a Bruker APEX-II diffractometer or a Bruker PHOTON-II using a combination of ω- and ϕ-scans of 0.5°.[39] The data were corrected for absorption and polarization effects and analyzed for space group determination.[40] The structures were solved by dual-space methods and expanded routinely.[41] The models were refined by full-matrix least-squares analysis of F2 against all reflections.[42] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded (U_{iso}(H) = 1.5U_{eq}(C) for methyl, 1.2U_{eq}(C) for all others). Tables of positional and atomic displacement parameters, bond lengths and angles, torsion angles and hydrogen bond contacts are in each crystallographic information file (CIF). Deposition Numbers 2152030, 2152031, 2152032, and 2152033 contain these data which are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service, www.ccdc.cam.ac.uk/structures. Shown in Table 1 is a summary of select crystal structure and refinement data, with additional details in the Electronic Supplementary Information.

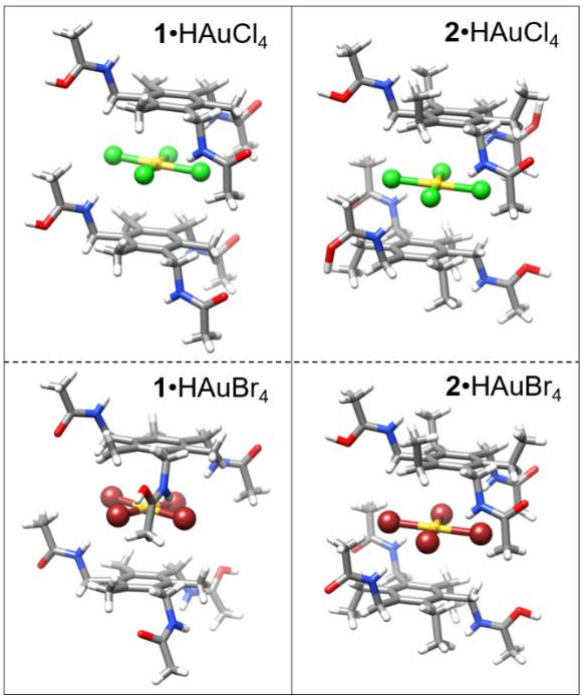


Figure 1. Comparison of the high energy tecton conformation and intermolecular orientation within each co-crystal structure.

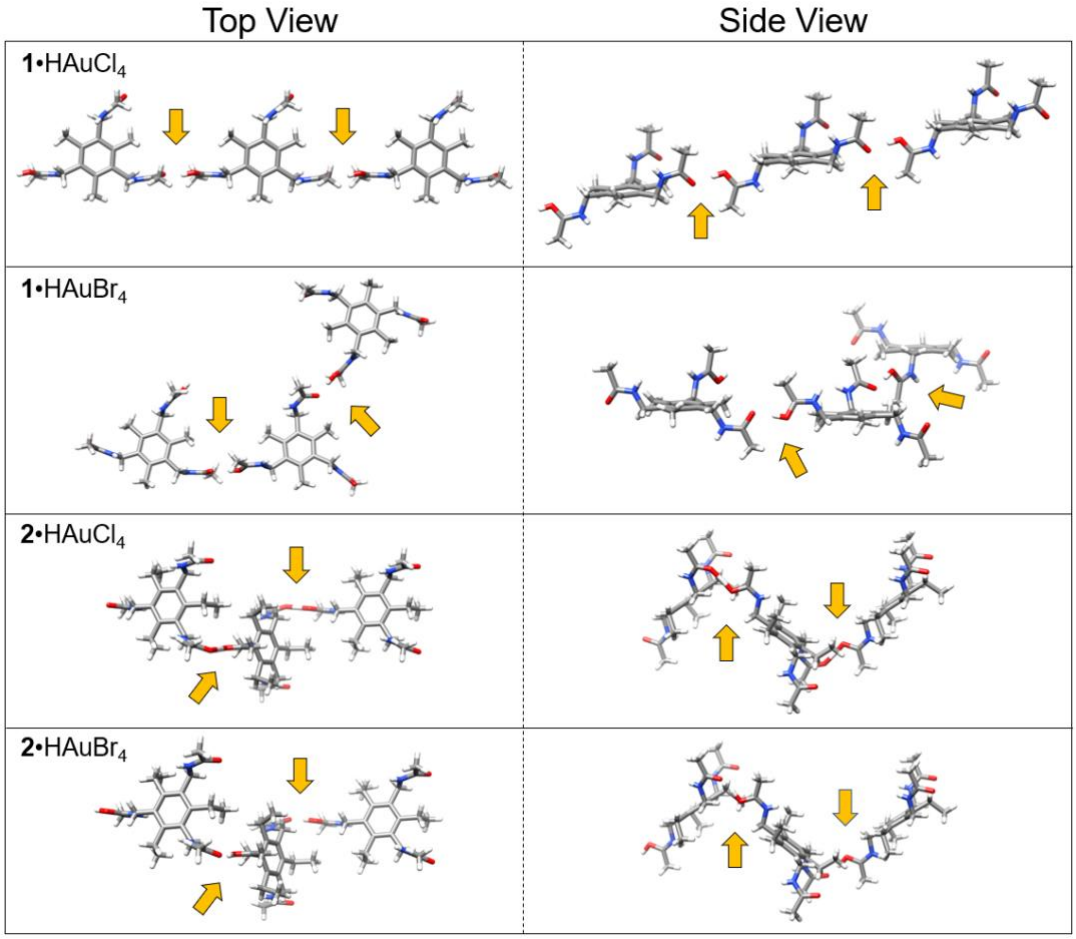


Figure 2. Comparison of the proton-bridged-carbonyls motif (CO···H⁺···OC) that creates a chain of linked organic tectons. Each picture shows three tectons linked by two CO···H⁺···OC bridges that are indicated by yellow arrows. The proximal AuX_4^- anions are removed for clarity.

Results and discussion

NMR spectra of the free compounds **1** and **2** in organic solution exhibited sharp peaks, consistent with a single, low energy conformation in solution with no evidence for slow conformational exchange.[43] Co-precipitation experiments were conducted by mixing separate solutions of **1** or **2** in $CHCl_3$ with equimolar amounts of $HAuCl_4$ or $HAuBr_4$ in dibutyl carbitol. The formation of a co-precipitate was virtually immediate in all cases, and recrystallization of each co-precipitate yielded single crystals suitable for analysis by X-ray diffraction.

Shown in Figure 1 is a comparison of molecular conformations and intermolecular orientations for the four different structures. In each co-crystal, the C3-symmetric tecton adopts the high energy conformation that is illustrated in Scheme 1. That is, for **1**•$HAuCl_4$ and **1**•$HAuBr_4$, the conformation of **1** is *ddu*, with two methylacetamide substituents directed "down" and one directed "up", and in the case of **2**•$HAuCl_4$ and **2**•$HAuBr_4$, the conformation of **2** is *uuudud*. In all co-crystals, at least half of the AuX_4^- anions are sandwiched between two aryl rings with the electron deficient Au center stacked against the aromatic surfaces indicating Au···π interactions. Unsurprisingly, the distance between the parallel aromatic rings in the two $AuCl_4^-$ structures (7.07 and 7.28 Å) is smaller than the corresponding distance in the two $AuBr_4^-$ structures (7.31 and 7.55 Å). The structures also indicate NH···X hydrogen bonding between tecton amide NH residues and the AuX_4^- anion (more specifically, there are three NH residues directed into the cavity for **1**•$HAuX_4$ and four NH residues directed into the cavity for **2**•$HAuX_4$).

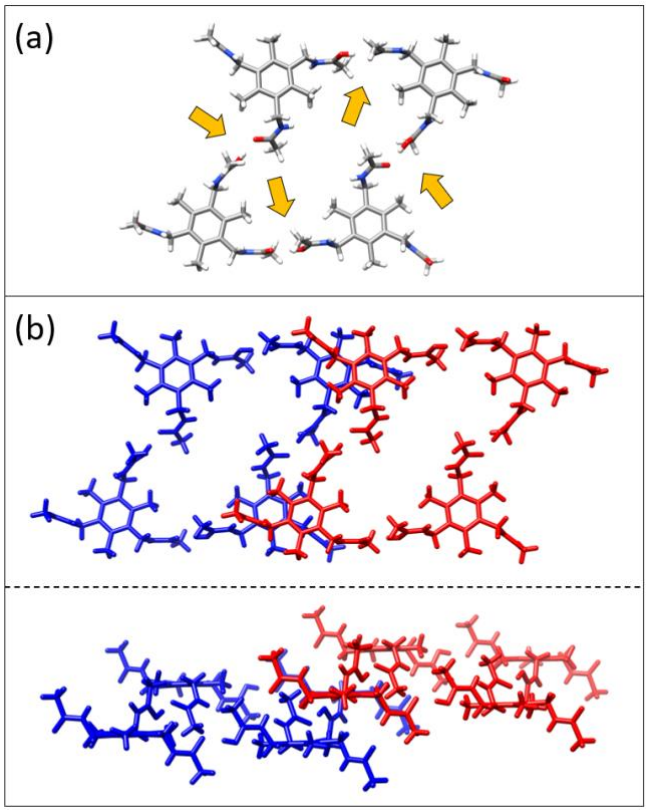
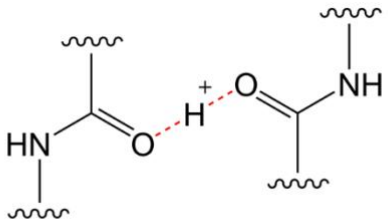


Figure 3. Additional representations of the arrangement of **1** within the co-crystal of **1**•$HAuBr_4$; (a) Four copies of **1** are linked by three CO···H^+···OC bridges (indicated by yellow arrows) as a non-covalent macrocycle. (b) Top and side views of two adjacent non-covalent macrocycles. The proximal $AuBr_4^-$ anions and solvent molecules are removed for clarity.

Table 2. Crystal structure bond distances for the three amide carbonyl groups within each organic tecton and illustration of relevant bonds



	C=O	C-N	CO···OC[c]
1•$HAuCl_4$	1.267(6)[a]	1.311(6)[a]	2.429(3)
	1.222(5)[b]	1.342(5)[b]	
1•$HAuBr_4$	1.26(5)[a]	1.30(4)[a]	2.42(3)
	1.24(2)[b]	1.34(3)[b]	
2•$HAuCl_4$	1.270(3)[a]	1.314(3)[a]	2.436(2)
	1.240(2)[b]	1.334(2)[b]	
2•$HAuBr_4$	1.270(4)[a]	1.310(4)[a]	2.452(2)
	1.236(3)[b]	1.336(3)[b]	

[a]Average for the two tecton amide carbonyls that are within a proton-bridged-carbonyls motif.
[b]Tecton amide carbonyl not in a proton-bridged-carbonyls motif.
[c]Average intermolecular oxygen-oxygen distance for all proton-bridged-carbonyls motifs in the co-crystal.

As expected, the average NH···X distance for the two $AuCl_4^-$ structures is ~2.8 Å and shorter than the ~3.0 Å for the two $AuBr_4^-$ structures. Further details about the NH···X H-bonding can be found in Table S1.

The third dominant non-covalent interaction that is present in all four co-crystal structures is the proton-bridged-carbonyls motif (CO···H^+···OC) that creates a chain of linked tectons.[44–47] The comparison in Figure 2 illustrates two key topological points: (a) two of the three carbonyls within each organic tecton are engaged in CO···H^+···OC bridges that create linear polymeric chains; (b) the shape of the linked chain changes with each co-crystal: it is relatively straight in **1**•$HAuCl_4$, highly bent in **1**•$HAuBr_4$, and "zig-zag" in the iso-structural co-crystals of **2**•$HAuCl_4$ and **2**•$HAuBr_4$.[48] The highly bent shape of the polymeric chain in **1**•$HAuBr_4$ is especially interesting in that it produces a solid-state macrocycle composed of four copies of **1** linked by four CO···H^+···OC units. Shown in Figure 3 is a picture of this non-covalent macrocycle (lacking the proximal $AuBr_4^-$ anions and solvent molecules) along with two partial views of the solid state stacking. These pictures suggest that the proton-bridged-carbonyls motif could be a productive new way to connect tectons that are derivatives of 1,3-bis(methylacetamide)benzene and create new classes of porous co-crystals.[49]

As stated above, two of the three amide carbonyls within each organic tecton (**1** or **2**) are engaged in CO···H^+···OC bridges, while the third carbonyl forms "regular" hydrogen bonds. This rare circumstance provides an opportunity to compare the impact of the proton-bridged-carbonyls motif on different amide groups within the same molecule. The bond distances listed in Table 2 are quite different and indicate that the two amide groups within the proton-bridged-carbonyls motif are more polarized than the third regular amide in the same molecule. Specifically, the average distance of the C=O bond is longer while the average C-N distance is shorter, indicating that the proton-bridged-carbonyls motif promotes a

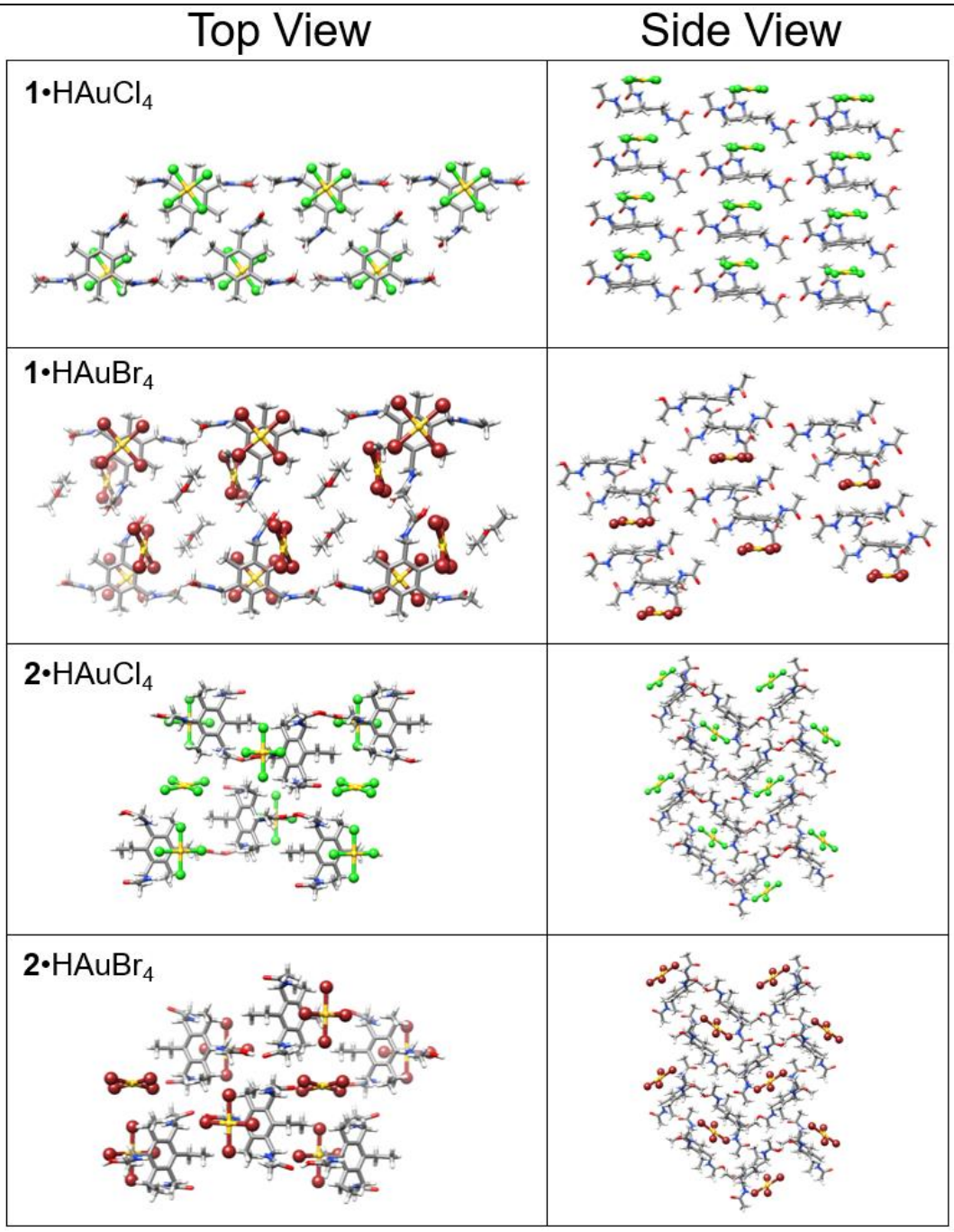


Figure 4. Top and side views of selected regions of the four co-crystal lattices. Solvent removed for clarity in the side view of **1**•$HAuBr_4$.

higher fraction of dipolar resonance contributor within the participating amides.[35] Also listed in Table 2 are the intermolecular CO···OC distances for all proton-bridged-carbonyls motifs in each co-crystal. In all cases, the CO···OC distance is < 2.5 Å, which is unusually short and likely is a strongly stabilizing solid-state interaction.[50]

Provided in Figure 4 are broader and more detailed comparative views of the lattice packing for each co-crystal. The lattice structure of **1**•$HAuCl_4$ is quite similar to that previously reported for co-crystals of $HAuCl_4$ and a C2-symmetric tecton.[35] There is continuous alternating stacking of $AuCl_4^-$ sandwiched between tecton **1** to create infinite columns, and the columns are bridged by proton-bridged-carbonyls motifs to create a sheet. Two opposing sheets form a bilayer which is continuously layered to produce the lattice. The lattice structure of **1**•$HAuBr_4$ can also be deconstructed as layers of bilayers but with a difference; the columns within the bilayers are an alternating stack of $AuBr_4^-$ and tecton **1** with 1:2 stoichiometry. The isostructural lattices of **2**•$HAuCl_4$ and **2**•$HAuBr_4$ cannot be deconstructed as layers of bilayers, rather they adopt complicated packing arrangements that include one dimensional polymers packed in "zig-zag" orientations. It is worth noting that only in the case of **1**•$HAuCl_4$ are all Au centers directly located over the center of the aryl rings. In the other three co-crystals, half of the AuX_4^-

anions are not located over aryl rings but rather they are positioned within interstitial voids. This suggests that the Au···π interaction is relatively weak and only occurs when it is combined with a simultaneous and cooperative NH···X hydrogen bond. This rationalization is consistent with a recently reported X-ray structure of $HAuCl_4$ mixed with an aryl tertiary amide; the tecton structure lacked NH residues and there were no close contacts between the Au center and the aryl π-electrons.[51]

Conclusions

The results of this study confirm our previous report that relatively simple aryl acetamide compounds are excellent co-precipitation agents for efficient removal of $HAuCl_4$ or $HAuBr_4$ from organic solution and that co-crystals are readily formed.[35 52] In all cases, X-ray analysis of the co-crystals reveals the presence of three dominant supramolecular interactions; (a) hydrogen bonding between tecton amide NH residues and the AuX_4^- anion, (b) electrostatic stacking of the Au center against the tecton's π-electrons, (c) very short hydrogen bonds within a proton-bridged-carbonyls motif. The role of electrostatics within each of these supramolecular interactions is likely to be important because crystalline environments often favor salt-forms over uncharged hydrogen bond structures.[53–55]

The organic tectons **1** and **2** are sterically-geared molecules with three methylacetamide substituents on a central aryl ring in a 1,3,5-orientation, and within all four co-crystals the tecton is trapped in a high energy molecular conformation. Wang and Hof have calculated the intramolecular energy difference for low and high energy conformations of 1,3,5-trialkylbenzene scaffolds.[18] Applying their data to the co-crystals of **1**•$HAuXl_4$, the ΔG for conversion of the lowest energy conformation for **1** (*ddd*) into the observed high energy conformation (*udd*) is ~1 kcal/mol, and for co-crystals of **2**•$HAuXl_4$, the ΔG for conversion of the lowest energy conformation of **2** (*udududud*) into the observed high energy conformation (*uuudud*) is ~4 kcal/mol (Figure S17). Solid state trapping of these high energy conformations is feasible since the corresponding energies are smaller than the estimated maximum distortion energy of ~5 kcal/mol that can be induced by crystal packing forces.[9]

Our results agree with a postulate by Thompson and Day that "*crystallization often selects high energy conformers, but only when the high energy conformer is more extended than the lower energy options, allowing for greater intermolecular stabilization*."[9] In the context of the present study, the low energy molecular conformations of organic tectons **1** (*ddd*) and **2** (*udududud*) are convergent structures, with all three methylacetamide substituents directed to the same face of the aryl scaffold. In contrast, the high energy molecular conformations of **1** (*udd*) and **2** (*uuudud*) direct one of the methylacetamide substituents in an opposite direction; an extended conformation that increases intermolecular stabilization of the lattice by the three dominant non-covalent interactions listed above. Thus, our results suggest a corollary of the Thompson and Day postulate; the likelihood of high energy molecular conformations within a co-crystal increases if there are multiple dominant intermolecular interactions. We expect that this corollary can be applied for improved co-crystal structure prediction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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