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Macrocyclic and acyclic supramolecular elements for co-precipitation of square-planar gold(III) tetrahalide complexes

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Abstract

Macrocyclic hosts have long been used for guest encapsulation, and recently a new application has emerged; employment as supramolecular elements for capture and recovery of gold through host/guest co-precipitation. The guests are square-planar tetrahaloaurate anions, practically important gold complexes with a capacity to engage in non-covalent interactions such as hydrogen bonding and Au-π interactions. The successful macrocyclic hosts for co-precipitation include cyclodextrins, cucurbiturils, and cyclophanes; with recent expansion of the structural scope to include acyclic amides.

Introduction

For most of civilization, gold has been highly prized as a precious metal for jewelry or currency, and more recently it has been incorporated into advanced industrial technologies such as catalytic chemistry and telecommunication devices. The combination of increasing demand and limited supply has elevated the need for more efficient and environmentally benign methods of mining gold or recovering it from secondary sources.[1–4] The most common large-scale method for mining gold ore is heap leaching. Typically, aqueous sodium cyanide is used as the lixiviant to convert the gold within the ore into a water-soluble and highly stable $Au(CN)_2^-$ complex. The gold-bearing aqueous solution is subsequently collected and treated to retrieve the gold metal. This cyanidation process is an efficient way to combine gold oxidation with cyanide coordination.[1] However, gold cyanidation is not effective with all gold ores, especially ores containing high amounts of sulfide minerals. Another major concern with gold cyanidation is environmental safety since sodium cyanide is a highly toxic chemical.[1,3,5] Although modern heap leaching incorporates best practices that promote safe and responsible use of sodium cyanide, there is nonetheless a non-zero risk that an unexpected spill could occur and produce a deadly exposure. Because of this concern, some regions of the world have banned the use of cyanide in mining operations.[1] Cyanidation is also used for recycling purposes, but it is not well suited for complicated, multistep recycling processes such as recovery from electronic waste. In these cases, the gold is present in very low amounts and often combined with other metals which increases the complexity of the work-flow and the risk of a personnel exposure.[2,6]

Over the years, many alternatives to cyanide have been investigated as gold lixiviants, including thiourea, thiosulfate, and the various halides. Though none of these leachants form gold complexes with the same high stability as $Au(CN)_2^-$ they each have useful attributes for effective gold recovery under the right conditions.[1,3,5] Chloroauric and bromoauric acid ($HAuX_4$) are especially attractive intermediates for gold separation because they can be formed by relatively simple procedures such as dissolving in *aqua regia*, which is a mixture of concentrated nitric and hydrochloric acids. However, the moderate lability of these tetrahaloaurate complexes requires the use of pH-controlled HCl or HBr solutions during the recovery to ensure that the desired $HAuX_4$ is the major species.[1,3]

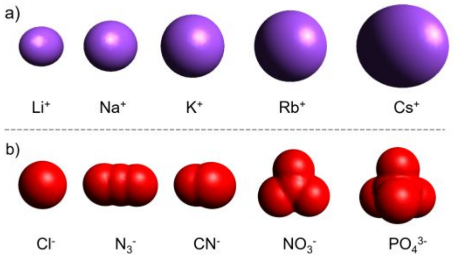
Broadly speaking, there are three distinct methods for $HAuX_4$ recovery: liquid-liquid extraction, solid-liquid adsorption, and co-precipitation. Liquid-liquid extraction uses an industrial organic solvent such as methyl isobutyl ketone or dibutyl carbitol to extract the gold complex from an aqueous carrier solution.[7] $HAuCl_4$ and $HAuBr_4$ are lipophilic molecules and can be extracted directly into an organic solvent. $HAuCl_4$, for example, has a distribution coefficient of 5,000-10,000 when extracted from concentrated HCl into dibutyl carbitol.[7] Extraction into less efficient organic solvents can be enhanced by the presence of organic soluble extractants such as quaternary ammonium cations or amide-based molecules which can interact with $HAuX_4$ through Coulombic attractions and hydrogen bonding.[8] [9] It is challenging, however, to develop large-scale liquid-liquid extraction as a safe and environmentally sound industrial technology, and there is a specific need for effective methods to remove all the gold from the organic phase so it can be recycled for additional extractions.[3] [7]

An example of solid-liquid adsorption is carbon-in-pulp, one of the common gold recovery methods used in conjunction with heap leaching. Activated carbon is added to the gold leaching solution in order to adsorb the gold coordination complex and enable collection by simple filtration. Although the method is useful, there is unselective adsorption which means that impurities are captured along with the gold.[1] Also, it is difficult to completely remove the captured gold complex from the activated carbon. The classical inorganic chemistry approach to enhance adsorption selectivity for gold cations is to exploit coordination chemistry. That is, to develop polymeric materials with surfaces comprised of chelating molecules that form metal-coordination bonds.[10–12] While resin capture methods are attractive for detection technologies, they are harder to implement as a large-scale recovery process due to major limitations concerning throughput volume and to environmental concerns with resin production and disposal.[13] A conceptually new approach to solid-liquid adsorption is to use a metal-organic framework (MOF), a rigid porous material with an infinite lattice composed of organic ligand coordinated to metal ions, or a covalent organic framework (COF), which is a lattice composed only of light elements held together by covalent bonds. Lattice structures with gold coordinating atoms produce MOF or COF materials that can remove gold from dilute solutions, even in the presence of much greater amounts of competing ions.[9,14–17] Thus, porous materials are promising for niche applications, but it is hard to envision their use for large-scale gold recovery processes.

The third possible approach to gold recovery is co-precipitation, an attractive but under-explored approach which combines phase separation and purification in a single step. In short, addition of a suitably designed co-precipitation molecule to a solution of gold complex instantly produces an insoluble supramolecular complex that is collected by filtration.[18] Subsequent processing of the co-precipitate provides the purified gold. In principle, co-precipitation has several favorable attributes as a new type of "green" gold recovery method. The time frame for a co-precipitation process can be very short even when it is conducted on a large scale. If the gold removal is quantitative, there is an opportunity to recycle the mother liquor without a major energy cost. The environmental impact is further lowered if the co-precipitation molecule is derived from a cheap and renewable resource.[18] A major reason for the current lack of efficient gold co-precipitation technology is the scarcity of supramolecular host molecules that recognize the gold complexes by weak non-covalent interactions. However, this situation is rapidly changing with the recent discovery of several supramolecular systems that selectively capture tetrahaloaurate complexes. This Highlight Article describes recent reports of organic host molecules for co-precipitation of tetrahaloaurate complexes and thus differs from previous reviews which focus on the inorganic chemistry or physical chemistry underlying the separations.[2,4] We summarize the underlying supramolecular paradigms that enable the non-covalent association, with the expectation that these paradigms can be used in the future for designing next-generation molecular hosts with customized AuX_4^- self-assembly and co-precipitation properties.

Molecular Recognition and Co-precipitation of AuX_4^-

Macrocycles have long been used for the encapsulation of ions. The discovery of crown ethers and cryptands in the 1960s was followed by a productive period of structure/affinity research that synthesized a wide range of macrocyclic structures and measured affinities for cations, anions, and neutral guest molecules. A guiding design rule is Cram's principle of preorganization which states: *the more highly hosts and guests are organized for binding and low solvation prior to their complexation, the more stable will be their complexes*.[19] A major outcome of this large body of work is a rich array of macrocyclic hosts that are endowed with the correct stereoelectronic properties to select between spherical metal cations with tiny differences in ionic radius, or anions that vary in molecular shape (Scheme 1).



Scheme 1. Shapes and sizes of a) Alkali metal cations, and b) Common anions. In each case, a macrocyclic host has been developed to selectively encapsulate the ion.

Here the supramolecular focus is on the molecular recognition of $HAuCl_4$ and $HAuBr_4$. They are strong acids and shown in Figure 1 are structures of the conjugate bases which are partially labile anionic complexes in aqueous solution. $AuCl_4^-$ is the dominant species in concentrated HCl, but the formation of $AuCl_3OH^-$ begins to occur as the solution approaches neutral or high pH.[20] Thus, aqueous recovery solutions of $AuCl_4^-$ need to be maintained at pH values below 3. In comparison, $AuBr_4^-$ is more stable and aqueous recovery solutions can be in the range of pH 5-8.[1] $AuCl_4^-$ and $AuBr_4^-$ are square planar anions with Au-X bond lengths of 2.28 Å for $AuCl_4^-$ and 2.42 Å for $AuBr_4^-$, respectively. Calculations of the charge distribution for each AuX_4^- ion indicate a partial positive charge on the gold center and partial negative charge on each of the four equivalent X ligands.[21]

From a host/guest design perspective, $AuCl_4^-$ and $AuBr_4^-$ can be viewed as square planar, charge-diffuse guest anions with four X ligands available for hydrogen bonding interactions with a molecular host (H). [21] [22] The counter cation within a co-precipitate depends on the pH and sample origin, but most often it is either H^+, Na^+ or K^+. The charge-diffuse $AuCl_4^-$ and $AuBr_4^-$ anions have relatively low hydration energies so ion-pairing with an added lipophilic cation is a simple way to induce co-precipitation from water. The problem with this obvious method is the formation of impure co-precipitates in real world samples that are complicated mixtures. A more sophisticated and potentially more practical supramolecular approach to devise a host molecule that can capture both ions and form a ternary, ion-pair complex $(M^{+}\bullet H\bullet AuX_4^{-})_4$ that prefers the crystalline solid state. In this case, the host molecule should be designed to have two major supramolecular features. One feature is the capability to capture the hydrated, charge-dense counter cation (H^+, Na^+ or K^+) and convert it into a lipophilic cation for ion pairing with the lipophilic AuX_4^-. The other feature is the capability to stabilize $(M^{+}\bullet H\bullet AuX_4^{-})$ in the solid state as a polymeric supramolecular network with strong directional non-covalent interactions such as hydrogen bonds. A polymeric bonding network can stabilize the early stages of $(M^{+}\bullet H\bullet AuX_4^{-})$ self-assembly and promote the formation of high purity co-crystals.

The following sections describe four classes of host molecules that have recently been shown to co-precipitate ion-pairs containing $AuCl_4^-$ or $AuBr_4^-$. The four host molecules are cyclodextrins (CD), cucurbiturils (CB), cyclophanes and acyclic amides. In each case, the co-precipitates have been characterized by X-ray crystallography and the results are analyzed here with a focus on the major non-covalent interactions that drive the host/guest assembly and lattice packing.

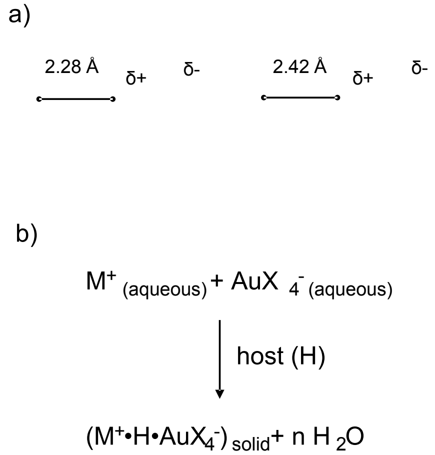


Figure 1. a) Ball and stick representations of $AuCl_4^-$ (left) and $AuBr_4^-$ (right). b) Addition of host molecule, H, induces co-precipitation of tetrahaloaurate salts from water, where $M^+ = H^+$, Na^+ or K^+; and $AuX_4^- = AuCl_4^-$ or $AuBr_4^-$

Cyclodextrins

Cyclodextrins (CDs) are naturally occurring cyclic molecules composed of repeating glucopyranose units and the most common structures are called α-, β-, or γ-CD depending on whether they contain six, seven, or eight sugar units, respectively. The internal cavity of a CD host is hydrophobic and can accommodate non-polar guest molecules that have a complementary size. In addition, the hydroxyl groups on both rims of a CD host can participate in hydrogen bonding interactions. Guest capture by CDs can sometimes lead to the formation of supramolecular nanotubes. The capability of CD to capture and co-precipitate square-planar gold complexes was first reported by Stoddart and coworkers in 2013.[18] Serendipitously, they found that addition of α-CD to an aqueous solution of $KAuBr_4$ rapidly produced a 2:1 inclusion complex that co-precipitated from solution. Electron microscopy and atomic force microscopy images of the co-precipitate revealed self-assembled nanotubes and atomic level detail was gained by analyzing single crystals by X-ray diffraction. As shown in Figure 2, the nanotubes are linear superstructures with a hybrid composition of repeating α-CD molecules and a continuous chain of alternating $AuBr_4^-$ and $K(OH_2)_6^+$. The α-CD chain can be viewed as a repeating sequence of supramolecular head-to-head dimers with each dimer interface containing a cyclic array of hydrogen bonds between the secondary hydroxyl groups on the adjacent α-CD rims. Included inside each dimer interface is a $K(OH_2)_6^+$ that is stabilized by second sphere coordination. In addition, each $K(OH_2)_6^+$ is connected in opposite directions to an $AuBr_4^-$ anion by O-H···Br-Au hydrogen bonds that extend axially through the cavities of the adjoining α-CD molecules. The included $AuBr_4^-$ also forms stabilizing C-H···Br-Au interactions with the interior lining of the α-CD cavity. Subsequent co-precipitation studies varied the cation (Na^+, K^+, Rb^+, or Cs^+), the gold ligands (Cl or Br), and the host size (α-, β-, or γ-CD) and among 24 different aqueous mixtures co-precipitation occurred in only three solutions, all with α-CD. Single crystal X-ray diffraction analysis of twenty different adducts showed that well-ordered nanotubes were only obtained with $KAuBr_4$ and α-CD, demonstrating that this co-precipitation pair was uniquely complementary in terms of size, shape and electronics. The perfect match of $K(OH_2)_6^+$ within the α-CD supramolecular nanotubes permits a large continuous chain of hydrogen bonds that stabilize the nanotubes and explains why a mixture of α-CD and $KAuBr_4$ co-precipitates rapidly and with very high efficiency. In contrast, no other mixture of CD and $MAuX_4$ possesses the same stereoelectronic match of host/guest structures. Even though there is a very small structural difference between the association partners, self-assembly is less favorable; a fact that is apparent from the co-crystal structures which reveal the metal cations in lattice locations that are outside the CD cavities.[23]

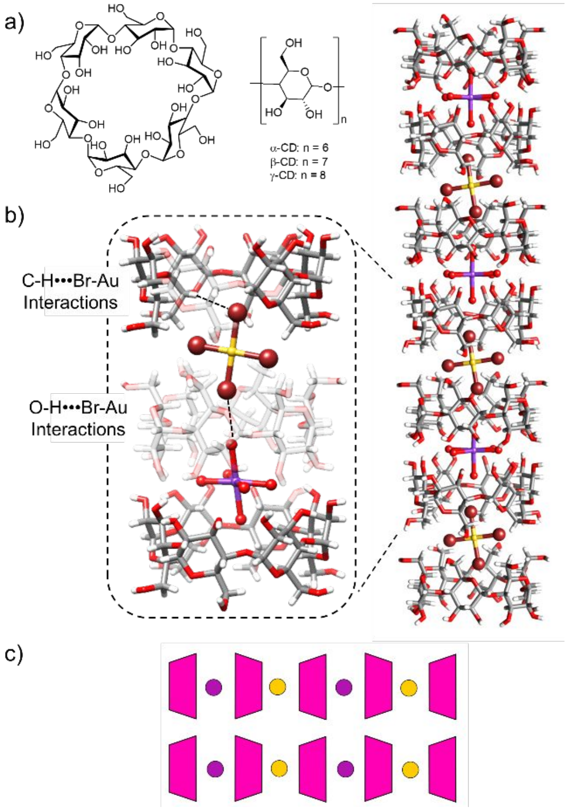


Figure 2. a) Structures of α-, β-, and γ-CD. b) X-ray crystal structure of α-CD • $KAuBr_4$ complex highlighting the major non-covalent interactions (left) and the solid-state nanotube superstructure (right). c) Simplified representation of lattice packing of nanotubes, with α-CD represented by pink trapezoids, $AuBr_4^-$ represented by yellow circles, and $K(OH_2)_6^+$ represented by purple circles.

Cucurbiturils

Cucurbiturils (CBs) are macrocycles composed of glycoluril repeating units. The number of these units present in the molecule is denoted by the number following the acronym, i.e. CB7 has seven glycoluril units.[24] These macrocycles have a hydrophobic cavity and a circular array of strongly polarized carbonyl groups that define each portal. As a result, CBs have very high affinities for hydrophobic cations that have a complementary size and shape to fit inside the CB cavity. In addition, metal cations are attracted to the cavity portals by ion-dipole interactions with the polarized carbonyl groups.[25] [26] CB5 and CB7 are more than an order of magnitude more water soluble than CB6 and CB8 apparently because they form more amorphous solid-state structures.[27] Even though CBs cannot encapsulate square planar $AuCl_4^-$ and $AuBr_4^-$, they are, nonetheless, quite effective as gold co-precipitation reagents. In 2019, a collaborative group of Chinese researchers showed that CB8 could co-precipitate $HAuCl_4$ from acidic media, and later expanded their studies to include the smaller analogues CB5, CB6, and CB7.[28,29] X-ray diffraction analysis of the CB8-derived co-crystals revealed honeycomb-like packing of the CB macrocycles with the $AuCl_4^-$ occupying the interstitial lattice sites (Figure 3). The co-crystals containing CB5, CB6, and CB7 exhibited similar packing features with the $AuCl_4^-$ contacting the CB outer surface by a mixture of ion-dipole and C-H···Cl-Au interactions.[30] There were some interesting differences in identity and location of the counter cation. With CB5, two H_3O^+ cations were bound to the opposing portals of each CB5 macrocycle; whereas, with CB6, the lattice H_3O^+ counter cations were more disordered. With larger CB7, the counter cation was $Au(H_2O)_4^{3+}$ encapsulated inside the macrocycle, an inclusion complex that is reminiscent of $K(OH_2)_6^+$ encapsulated by dimeric α-CD. Thus, there are different supramolecular ways to capture a charge-dense counter cation and stabilize it in the solid-state for ion-pairing with charge-diffuse AuX_4^-.

A related 2020 study by the Stoddart group showed that CB6 could very efficiently capture and co-precipitate $AuCl_4^-$ or $AuBr_4^-$ with H_3O^+ or K^+ as the counter cation.[31] The co-crystal structures showed variation in the lattice packing but, as above, the AuX_4^- anions were connected to the outside of the CB6 macrocycles by a mixture of ion-dipole and C-H···X-Au interactions. In acidic solutions that also contained K^+ there was a preference for the CB6•$AuCl_4^-$ co-crystals to include H^+ rather than K^+ as the counter-cation. In contrast, the same experiment with CB6•$AuBr_4^-$ produced co-crystals with half of the counter-cations as K^+. This suggests that the counter cations do not contribute much to the formation and stabilization of the lattice superstructures.

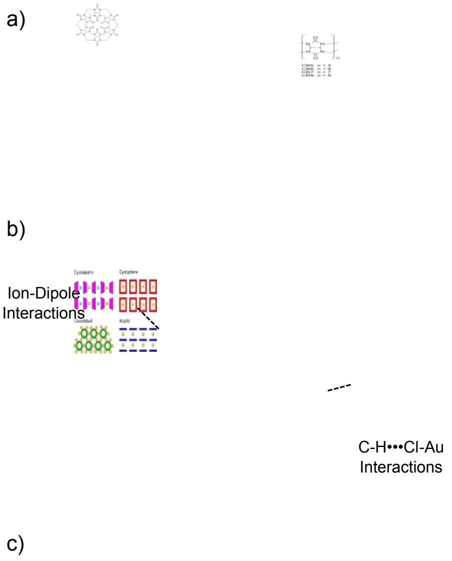


Figure 3. a) Structures of CB5-8. b) X-ray crystal structure of CB6 • $HAuCl_4$ complex highlighting non-covalent interactions. c) Simplified representation of lattice packing. CB[6] is represented by green hollow circles and $AuCl_4^-$ is represented by yellow circles. The disordered counter cations are not shown.

Cyclophanes

Cyclophanes are macrocyclic host molecules with aromatic sidewalls. The structure and properties and solubilities of cyclophanes can be readily varied by synthetic manipulation. Gong and coworkers prepared the tetracationic imidazolium cyclophane **1** in Figure 4 and evaluated its ability to capture and co-precipitate various anionic complexes of precious metals. In several cases they obtained single crystals suitable for x-ray diffraction, including a structure with $AuCl_4^-$. As shown in Figure 4, the cyclophane adopts a tweezer-like orientation that engages the $AuCl_4^-$ anion with a combination of Au-π and C-H···Cl-Au interactions. These weak interactions do not have strong directional preference or shape selectivity; rather, the co-precipitation process is driven primarily by the low polarity of the ion pair.[32]

A more precise AuX_4^- recognition system was developed by Smith and coworkers who showed that the tetralactam cyclophanes **2** and **3** in Figure 5 were stereoelectronically matched hosts for various precious metal complexes including square planar $AuCl_4^-$ and $AuBr_4^-$.[22] Addition of the cyclophanes to solutions of $HAuCl_4$ or $HAuBr_4$ in organic solvent instantly produced co-precipitates that led to X-ray crystal structures. The representative structure in Figure 5 shows that $AuCl_4^-$ is encapsulated by the surrounding tetralactam and stabilized by electrostatic Au-π and C-H···Cl-Au interactions, with hydrated H_3O^+ as the counter cation located outside the cavity.[22] Subsequent work by Jiang and coworkers found that a closely related tetralactam macrocycle could capture $AuCl_4^-$ in solution. Crystal structures were not obtained, but molecular modeling indicated that the same non-covalent recognition process was operating.[33]

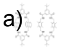


Figure 4. a) Structure of cyclophane **1**. b) X-ray crystal structure of **1** • $HAuCl_4$ complex highlighting the major non-covalent interactions.

Figure 5. a) Structures of cyclophanes **2** and **3**. b) X-ray crystal structure of **3** • $HAuCl_4$ complex highlighting the major non-covalent interactions. c) Simplified representation of lattice packing. Cyclophane **2** or **3** is represented by red hollow rectangles and $AuCl_4^-$ or $AuBr_4^-$ is represented by yellow circles. The hydronium counter cations are not shown.

Acyclic Amides

Very recently, the Smith group extended the supramolecular paradigm beyond macrocyclic tetralactams to include acyclic amide host molecules.[34] The practical motivation was to find structurally simple co-precipitation molecules that could be prepared cheaply on a large scale and also to develop low molecular weight systems that co-precipitated gold from aqueous mother liquors. They first prepared the two acyclic bis(amide) structures **4** and **5** shown in Figure 6 and found them to co-precipitate $HAuX_4$ from organic solvents. X-ray diffraction analysis of recrystallized versions of the co-precipitates revealed the expected stabilization of captured AuX_4^- anion by a combination of Au-π and C-H···X-Au interactions. Interestingly, the counter cation is a dehydrated H^+ bridged by two amide carbonyls ($CO\cdots H^+\cdots OC$), a relatively uncommon motif with very short hydrogen bonds ($CO\cdots OC$ distance < 2.5 Å). Furthermore, the proton bridged carbonyls motifs enables the formation of linear, one-dimensional polymers that stack in the solid-state to create sheets that are layered to create the three dimensional lattice.

Based on these results a new acyclic host molecule **6** was designed with one of the amides replaced by an amidinium group. This cationic host molecule was found to co-precipitate $HAuCl_4$ from aqueous media and X-ray diffraction analysis of a co-crystal showed the expected combination of Au-π and C-H···Cl-Au interactions. From the perspective of supramolecular design it is important to note that the central aromatic unit within these acyclic host molecules is a durene derivative (2,3,5,6-tetramethylbenzene) and its methyl groups enforce the adjacent amide or amidinium units to adopt a restricted set of molecular conformations that are pre-organized for favorable interaction with a guest AuX_4^- anion. In terms of practical potential, the ability to synthesize these simple acyclic compounds on a large scale, makes them very attractive for incorporation within next-generation gold recovery processes that employ co-precipitation. Although many different factors will determine if a specific host molecule will be successfully translated to industrial usage it is worth highlighting that one simple but important parameter to consider is the mass of the host molecule. The larger the host molecule and the higher its stoichiometric ratio in the co-precipitate means a higher mass of co-precipitation material needed for process operation and eventual disposal. In this regard, the data in Table 1 highlights the substantial mass advantage that is gained by using the acyclic amide **6** for gold co-precipitation from an aqueous solution.

Table 1. Host Molecular Weights and Co-Precipitation Stoichiometries.

Host	Molecular Weight	H:AuX_4^- Stoichiometry
α-CD	972	2:1
CB6	996	1:2, 1:3, 1:1, 2:5
1	624	1:1
2	845	1:1
3	757	1:1

4	276	1:1
5	388	1:1
6	310	1:1

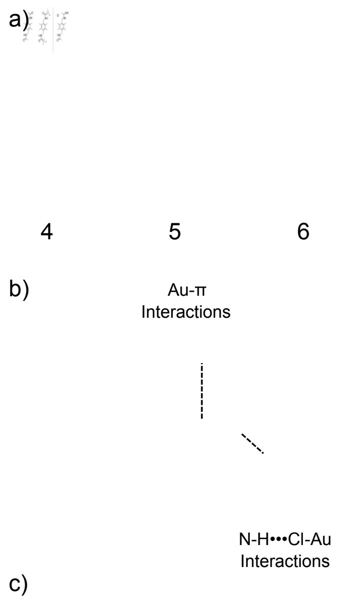


Figure 6. a) Structures of organic-soluble acyclic receptors **4** and **5**, and of water-soluble acyclic receptor **6**, b) X-ray crystal structure of **4** • $HAuCl_4$ complex highlighting non-covalent interactions c) Simplified representation of lattice packing. Acyclic host **4**, **5**, or **6** is represented by blue rectangles and $AuCl_4^-$ or $AuBr_4^-$ is represented by yellow circles.

Conclusion

Co-precipitation of gold complexes is emerging as a conceptually new approach to gold recovery that is informed by very recent and ongoing discoveries in host-guest chemistry using macrocycles and acyclic analogues. The successful gold co-precipitation systems outlined above clearly demonstrate that the rational design of complementary host/guest pairs as supramolecular elements can lead to reliable gold capture systems. This Highlight Article has focused on square planar, tetrahaloaurate anion (AuX_4^-) as the guest target, and described the major non-covalent interactions that drive the host/guest assembly and lattice packing. Eventual translation of these prototype systems to industrial operation will require much more extensive field testing. Not only must the successful candidates achieve separation performance benchmarks, such as high mass removal efficiency and gold selectivity, but they must meet also other selection criteria. These include important environmental requisites (e.g., no toxicity, short environmental lifetime of host molecule, ability to recycle the mother liquor) and economic factors (e.g., low-cost synthesis of host molecule, economic plant operation, and minimal waste disposal).

Looking to the future, it seems likely that the same supramolecular design principles can be applied to gold cyanide ($AuCN_2^-$) or other gold species ligated with more environmentally benign ligands such as thiourea or thiosulfate. Furthermore, co-precipitation has promise as a new method to recover the anionic complexes of other precious metals such as platinum or palladium. In addition to mining and environmental recovery, the underlying supramolecular paradigms may be exploited as new methods of precious metal self-assembly and nanofabrication for the production of advance materials, microelectronics, immobilized catalysts, and nanotechnology.

Conflicts of interest

There are no conflicts to declare

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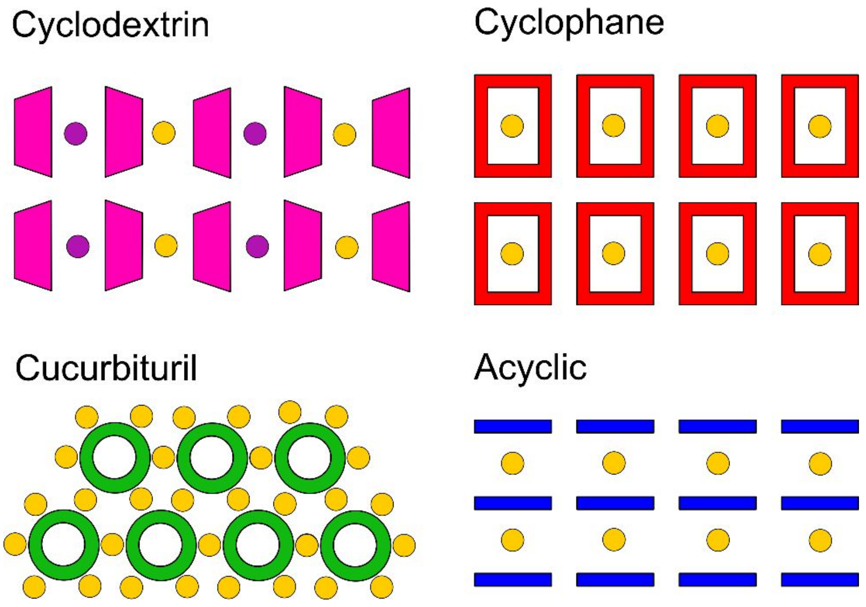
TOC Graphical Abstract



Non-covalent interactions control the solid-state packing of AuX_4^- anions (yellow circles) co-precipitated with different supramolecular elements

Author Photos and Biographies

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