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Macrocyclic Receptor for Precious Gold, Platinum, or Palladium Coordination Complexes

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Supporting Information

ABSTRACT: Two macrocyclic tetralactam receptors are shown to selectively encapsulate anionic, square-planar chloride and bromide coordination complexes of gold(III), platinum(II), and palladium(II). Both receptors have a preorganized structure that is complementary to its precious metal guest. The receptors do not directly ligate the guest metal center but instead provide an array of arene π-electron donors that interact with the electropositive metal and hydrogen-bond donors that interact with the outer electronegative ligands. This unique mode of supramolecular recognition is illustrated by six X-ray crystal structures showing receptor encapsulation of $AuCl_4^-$, $AuBr_4^-$, $PtCl_4^{-2}$, or $Pd_2Cl_6^{-2}$. In organic solution, the 1:1 association constants correlate with specific supramolecular features identified in the solid state. Technical applications using these receptors are envisioned in a wide range of fields that involve precious metals, including mining, recycling, catalysis, nanoscience, and medicine.

Metal ligation is often called first-sphere coordination and can be delineated from the supramolecular process of second-sphere coordination, which refers to non-covalent recognition of the outer ligands by a surrounding molecular receptor.[1−4] The concept of simultaneous first- and second-sphere coordination has been demonstrated using host molecules whose structures contain multiple heteroatoms that ligate a guest metal center (first-sphere coordination) and also form hydrogen bonds with the guest second-sphere ligands.[5−10] Here we describe a new way to selectively recognize a metal coordination complex using a macrocyclic receptor that does not directly ligate the metal center but instead surrounds the guest with an array of different non-covalent interactions. We show how this generalizable supramolecular strategy can be employed to encapsulate anionic, square-planar coordination complexes of precious metals, with a focus on the economically important chloride and bromide complexes of gold(III) and chloride complexes of platinum(II) and palladium(II).

The logic that that led to our receptor design is illustrated in Figure 1, which presents a side view of a square-planar MX_4^{n-} anion with polarized M−X bonds that have covalent character.[11,12] Surrounding the guest is a complementary macrocyclic receptor whose cavity is lined with a preorganized array of hydrogen-bond donors to interact electrostatically with the electronegative X ligands and arene π-electron donors to interact with the electropositive metal center.[13] This latter interaction is not the same as a classic metal cation−π interaction[14] because covalent bonding of the metal center to the X ligands attenuates the metal's charge and electron acceptor ability.[15] The first aim of the project was to create synthetic receptors for $AuCl_4^-$ and $AuBr_4^-$ with an eventual goal of developing new gold recovery processes as environmentally benign alternatives to current hydrometallurgical methods that use toxic cyanide salts to leach the gold from gold-bearing sources.[16−18]

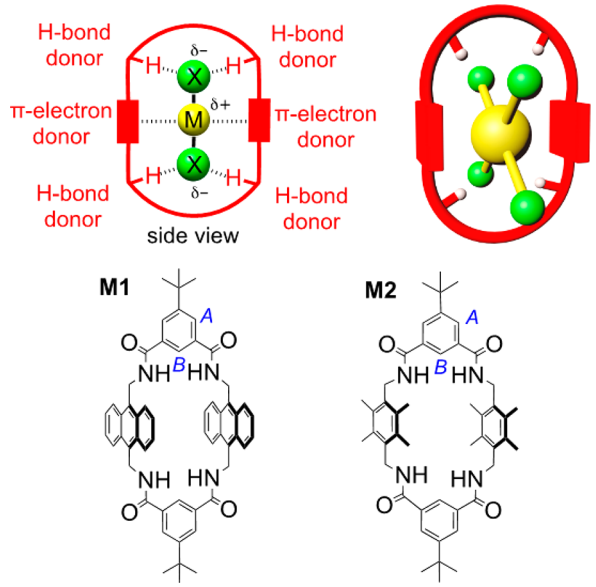

Figure 1. (top) Conceptual design of a macrocyclic receptor for square-planar MX_4^{n-} anions. (bottom) The two macrocycles used in this study.

Our previous experience with arene tetralactam macrocycles as supramolecular hosts for organic dyes[19−22] suggested to us that they may have the correct cavity size and mixture of functional groups to encapsulate a AuX_4^- guest. Therefore, we conducted preliminary studies using the known tetralactam **M1**.[21] A notable feature of this macrocycle is its structural preorganization, which keeps the amide NH residues directed inward even when the macrocycle is empty. Simple experiments in which $HAuCl_4$ or $HAuBr_4$ was mixed with **M1** in chloroform created an instant precipitate. Recrystallization of the

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complexes produced single crystals that were suitable for analysis by X-ray diffraction. The two crystal structures in Figure 2 are isostructural and show the $AuCl_4^-$ or $AuBr_4^-$

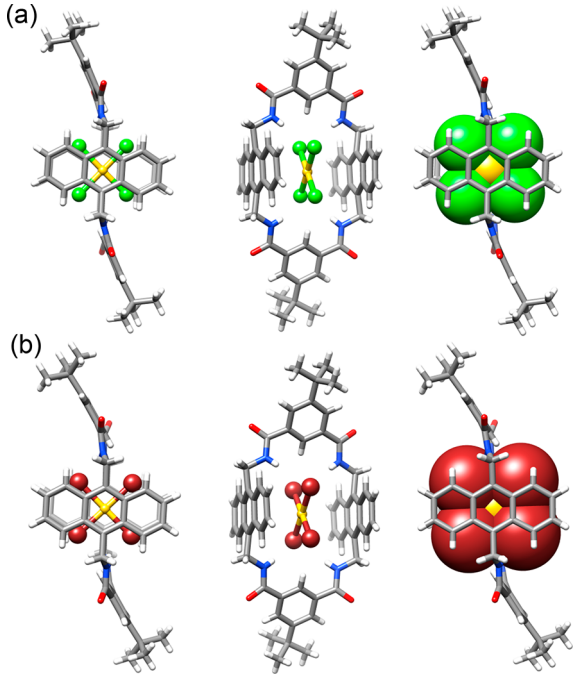

Figure 2. Different views of the X-ray crystal structures of (a) **M1**·$AuCl_4^-$ and (b) **M1**·$AuBr_4^-$. Hydronium countercations have been omitted for clarity.

inside the receptor cavity with an external hydronium countercation. The Au(III) center is located between the two parallel anthracene sidewalls of the receptor, which are separated by 7.298 Å for $AuCl_4^-$ and 7.487 Å for $AuBr_4^-$. In each case, a reduced density gradient (RDG) analysis indicated favorable van der Waals interactions between the Au(III) center and the receptor anthracene sidewalls.[23,24] Although Au···π-electron interactions are well-documented,[13,25−27] these structures appear to be the first discrete supramolecular complexes with a gold center symmetrically sandwiched between two parallel arene faces. Each pair of NH amide residues within the symmetrical macrocycle cavity forms bifurcated hydrogen bonds with the outer Cl or Br ligands. In the $AuCl_4^-$ complex, the average Au−Cl bond length is 2.282 Å and the average NH···Cl distance is 2.985 Å. In the $AuBr_4^-$ complex, the average Au−Br bond length is 2.419 Å and the average NH···Br distance is 3.054 Å. Not only do the Cl or Br ligands engage in weak hydrogen bonds with the receptor NH residues, but there are also close contacts with the receptor isophthalamide protons *B* (2.921 Å for the $AuCl_4^-$ complex and 2.989 Å for the $AuBr_4^-$ complex). It is notable that receptor **M1** can encapsulate $AuCl_4^-$ or the larger $AuBr_4^-$ without any major change in receptor conformation. This is the case because the receptor NH bonds lie on a plane that is orthogonal to the plane of the Au−X bonds, and thus, the guests of different sizes can be accommodated inside the receptor cavity without causing undesired strain or repulsive interactions.

The solution-state binding properties of **M1** were conveniently measured by conducting ^{1}H NMR titration experiments in $CDCl_3$ using soluble tetrabutylammonium (TBA^+) salts. The titration studies added aliquots from separate stock solutions containing $TBA^+\cdot Cl^-$, $TBA^+\cdot AuCl_4^-$, and $TBA^+\cdot AuBr_4^-$. The gold salt titrations produced large downfield changes in chemical shift for the receptor NH residues and protons *B*, which is a diagnostic indicator of guest encapsulation inside the receptor cavity. In each case, the titration isotherm was fitted to a 1:1 binding model, and independent support for the 1:1 complex was gained by observing intense molecular ion peaks in the high-resolution electrospray ionization mass spectrum. The values of K_a for receptor **M1** in Table 1 have the following order of guest affinities: $AuCl_4^-$ > $AuBr_4^-$ > Cl^-.

Table 1. Association Constants K_a (M^{-1}) in $CDCl_3$ at 25 °C

	receptor	
guest[a]	**M1**	**M2**
Cl^-	90 ± 7	24 ± 2
$AuCl_4^-$	923 ± 49	(7.8 ± 1.9) × 10^4
$AuBr_4^-$	187 ± 5	(2.5 ± 0.2) × 10^3
$PtCl_4^{2-}$	–	20 ± 4
$Pd_2Cl_6^{2-}$	–	(3.8 ± 0.4) × 10^3

[a]Tetrabutylammonium as the countercation.

In order to increase the affinity and selectivity for AuX_4^- guests, we designed and prepared a new tetralactam receptor, **M2**, with two 2,3,5,6-tetramethylbenzene (durene) sidewalls. Computer modeling indicated that the electrostatic potential at the center of the arene sidewalls in **M2** is more negative than that in **M1** (Figure 3), and thus, **M2** should be able to interact

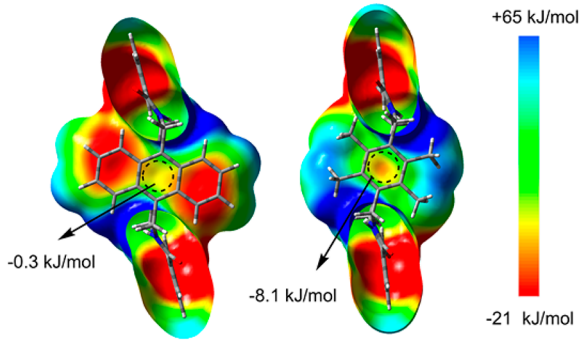

Figure 3. Electrostatic potential maps of the interior surfaces of (left) **M1** and (right) **M2** obtained by DFT calculations at the B3LYP/6-31G* level with the crystal structures as input.

more strongly with the electrophilic gold center of an encapsulated AuX_4^-.[28] Moreover, the cavity of **M2** is surrounded by a ring of positive electrostatic potential that can interact with the guest's electronegative X ligands. In addition, we expected the four methyl groups on each durene side wall in **M2** to enhance the guest affinity by promoting a highly preorganized macrocyclic structure with inward-directed NH residues. This structural feature was confirmed by an X-ray crystal structure of free **M2** showing parallel durene sidewalls and a cavity containing two hydrogen-bonded DMSO solvent molecules (Figure 4a).

Figure 4b,c shows X-ray crystal structures of the supramolecular complexes produced by mixing **M2** with $TBA^+\cdot AuCl_4^-$ and $TBA^+\cdot AuBr_4^-$, respectively. The complexes are isostructural and encapsulate the $AuCl_4^-$ or $AuBr_4^-$ guest inside **M2** with an external TBA^+. As above, the Au(III) center is

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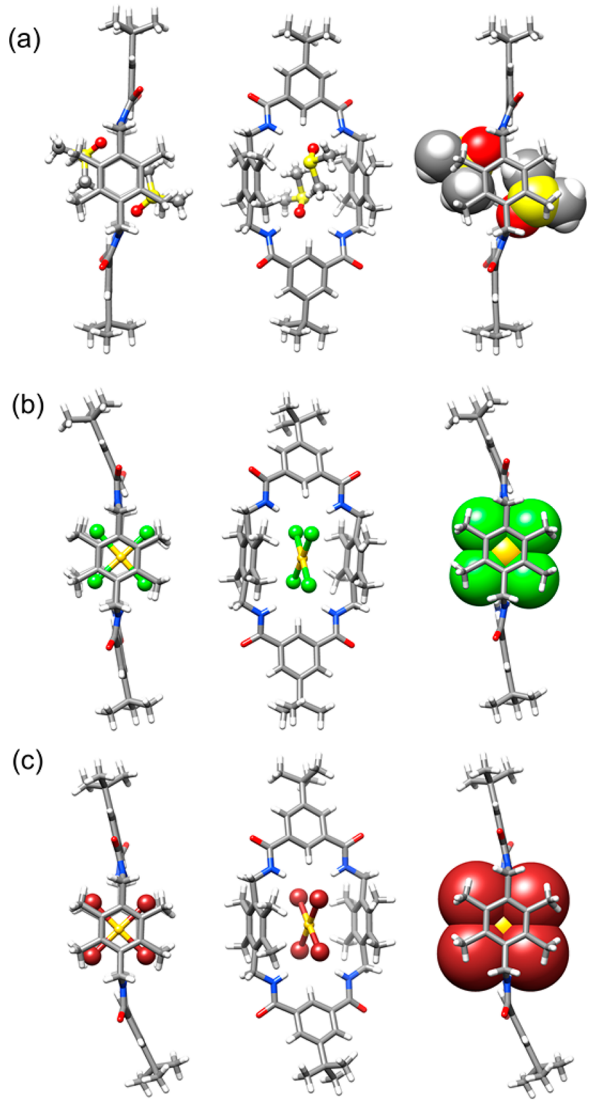

Figure 4. Different views of the X-ray crystal structures of (a) **M2**·2DMSO, (b) **M2**·$AuCl_4^-$, and (c) **M2**·$AuBr_4^-$. Tetrabutylammonium countercations have been omitted for clarity.

symmetrically sandwiched between the two parallel durene sidewalls, which are separated by 7.326 Å for $AuCl_4^-$ and 7.375 Å for $AuBr_4^-$. The receptor NH residues form weak bifurcated hydrogen bonds with the outer Cl or Br ligands. In the **M2**·$AuCl_4^-$ complex, the average Au−Cl bond length is 2.278 Å and the average NH···Cl distance is 2.889 Å. In the **M2**·$AuBr_4^-$ complex, the average Au−Br bond length is 2.420 Å and the average NH···Br distance is 2.936 Å. In addition to polar interactions with the receptor NH residues, there are close contacts with the receptor protons *B* and methyl CH residues. In each case, a single X residue on an encapsulated AuX_4^- is surrounded by an arched array of two NH and five CH residues.

^{1}H NMR titration experiments were conducted using **M2** in $CDCl_3$. We were pleased to find that the K_a values for binding of $AuCl_4^-$ and $AuBr_4^-$ were each increased by a factor of 10, whereas the affinity for Cl^- was decreased by a factor of 4 (Table 1). One measure of the change in receptor selectivity is the ratio of K_a values for $AuCl_4^-$ and Cl^-, and this ratio is 10.6 for **M1** and 3607 for **M2**. This difference in receptor selectivity is attributed to the influence of the methyl groups on the durene sidewalls for **M2**, which induces opposite non-covalent effects on guest binding. In the cases of $AuCl_4^-$ and $AuBr_4^-$, guests that are completely encapsulated by the receptors, the durene methyl groups in **M2** provide stabilizing CH···XAu interactions. However, in the case of Cl^-, a guest that most likely perches outside the receptor cavity, the methyl groups in **M2** sterically inhibit hydrogen bonding with the receptor NH residues.

Beyond gold, several other very important precious metals are known to form anionic square-planar coordination complexes, and as a preliminary test of the versatility of **M2**, we evaluated its ability to encapsulate $PtCl_4^{2-}$ and $PdCl_4^{2-}$. Association studies used the corresponding chloroform-soluble TBA salts, which enabled crystallization and ^{1}H NMR titration experiments. The supramolecular results for $PtCl_4^{2-}$ were as expected. The solid-state structure of **M2**·$PtCl_4^{2-}$ (Figure 5a)

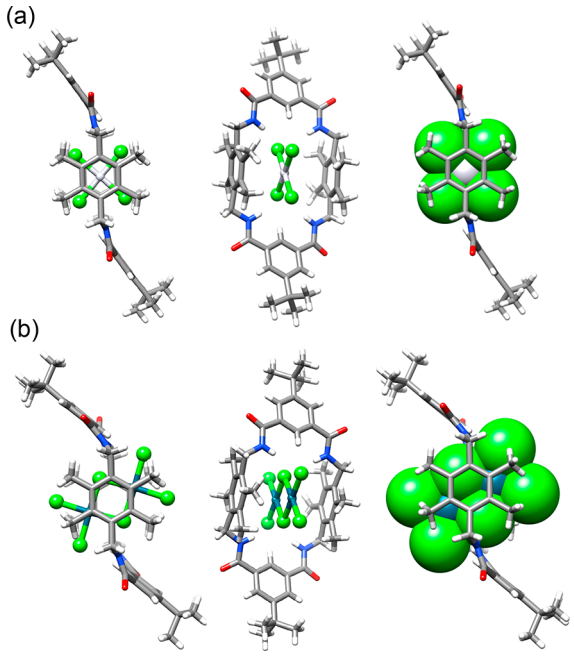

Figure 5. Different views of the X-ray crystal structures of (a) **M2**·$PtCl_4^{2-}$ and (b) **M2**·$Pd_2Cl_6^{2-}$. Tetrabutylammonium countercations have been omitted for clarity.

was very similar to the analogous gold structure above, with the exception of having two TBA cations in the lattice. The K_a for association of **M2** and $PtCl_4^{2-}$ was 20 ± 4 M^{-1}, reflecting the lower electrophilicity of Pt(II) compared with Au(III). The K_a for $PdCl_4^{2-}$ ((3.8 ± 0.4) × 10^3 M^{-1}) is much higher because the relatively labile $PdCl_4^{2-}$ forms a palladate dimer ($Pd_2Cl_6^{2-}$) under the experimental conditions of high concentration, weakly polar solvent, and diffuse countercation.[29−31] The solid-state structure of **M2**·$Pd_2Cl_6^{2-}$ in Figure 5b indicates attractive interactions between all six electronegative Cl^- ligands and the peripheral ring of positive electrostatic potential that surrounds the cavity of **M2** (Figure 3). We infer from these supramolecular results that receptor interactions with the guest metal center and the outer X ligands are both important factors that can influence the affinity. Furthermore, it is possible that these polar non-covalent interactions are cooperative.[32]

The supramolecular recognition strategy described here is a new way to reversibly encapsulate precious metal coordination complexes under mild conditions.[17,33] The simple macrocyclic

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structure is readily amenable to modifications that enable operation in different solvents (especially water)[34] or on the surface of solid supports. In addition to separation processes for precious metal mining,[16] recycling,[35−37] or water purification,[38,39] these new receptors will likely be useful for many other applications that involve precious metals, such as high-sensitivity detection,[40] catalysis and process chemistry,[41,42] magnetic materials,[43] nanoparticle fabrication,[44] and drug delivery.[45,46] Studies are ongoing, and the results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04155.

Chemical synthesis and characterization, NMR titrations, mass spectral data, X-ray crystal data, RDG analyses, and DFT calculations (PDF)
Crystallographic data for **M1**·$HAuCl_4$ (CIF)
Crystallographic data for **M1**·$HAuBr_4$ (CIF)
Crystallographic data for **M2**·2DMSO (CIF)
Crystallographic data for **M2**·TBA^+·$AuCl_4^-$ (CIF)
Crystallographic data for **M2**·TBA^+·$AuBr_4^-$ (CIF)
Crystallographic data for **M2**·$(TBA^+)_2$·$PtCl_4^{2-}$ (CIF)
Crystallographic data for **M2**·$(TBA^+)_2$·$Pd_2Cl_6^{2-}$ (CIF)

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Notes

The authors declare no competing financial interest.

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