

Supramolecular Recognition Forces: An Examination of Weak Metal–Metal Interactions in Host–Guest Formation

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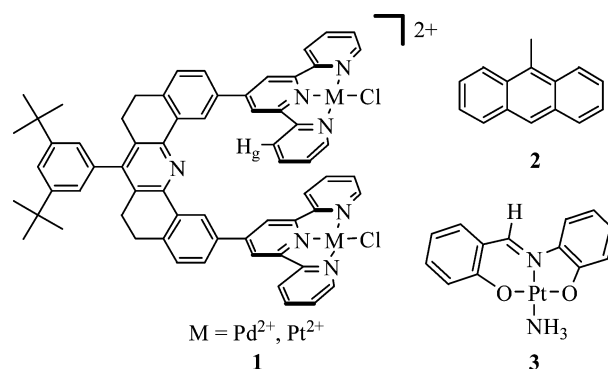
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Molecular receptors consisting of two parallel-disposed terpy–M–Cl units (M = Pd²⁺, Pt²⁺) are used to form host–guest adducts with aromatic molecules and with neutral square-planar Pt²⁺ complexes. Host–guest formation is controlled by several factors including π – π interactions and, in some cases, weak Pt–Pt interactions between the host and the guest. This latter interaction was examined by comparing the host–guest stability of adducts formed by isoelectronic Pt²⁺ and Au³⁺ complexes with the Pt²⁺ receptor. Consistently, the former is more stable.

Molecular receptors of the type **1** form host–guest adducts with a variety of planar aromatic molecules and square-planar metal complexes. With, for example, 9-methylanthracene, **2**, the yellow Pd²⁺ receptor forms a red 1:2 host–guest complex in CD₃CN solution at 27 °C, where one guest lies in the molecular cleft and the other resides on the outer faces of the terpy–Pd–Cl units.¹ This site occupancy of the guest is found in the solid state and is inferred from ¹H NOE spectra in solution.² The two microscopic³ stability constants were found to be 650 and 100 M^{–1}, the former constant referring to the guest residing in the molecular cleft.² We report here that the Pt²⁺ receptor under the same conditions also forms a structurally similar 1:2 host–guest adduct with **2** and that the two microscopic stability constants are essentially the same as those for the Pd²⁺ receptor, namely, 800 and 100 M^{–1}.

On the other hand, the light yellow platinum-based guest **3** forms bright red 1:1 host–guest adducts in dimethylformamide (DMF)-*d*₇ solution at 70 °C with both the Pd²⁺ and the Pt²⁺ receptors. The guest resides in the molecular cleft⁴ and forms stable adducts. For the Pd²⁺ receptor, the stability



constant⁴ is 2600 M^{–1}, and for the Pt²⁺ analogue, a value of 4100 M^{–1} was determined for the stability constant. Of special interest was the observation that, in the solid state, the Pt²⁺ receptor showed trimetallic Pt–Pt interactions with the guest **3**.⁴ These metal–metal interactions are preserved in solution.⁴

X-ray-diffraction-quality orange crystals of the Pt²⁺ receptor containing nine DMF molecules of crystallization were obtained from DMF solution by diffusion of isopropyl ether. The structure is shown in Figure 1, together with a schematic of the interplanar separations; the interplanar angles are given in parentheses. Note that the interplanar separations are those expected for π – π stacking⁵ (3.35–3.45 Å). In the crystal, the molecular structure consists of pairs of interlocking pairs of molecules with eight terpy–Pt–Cl units stacked on each other (see Supporting Information). The bond lengths and angles are unexceptional, but in order for the molecular clefts to achieve the observed separation of 6.785 Å, the two terpy–Pt–Cl units undergo a concerted twist about the spacer unit, which is in a racemic configuration.⁶ The Pt–Pt distances are greater than 3.7 Å indicating the absence of significant metal–metal interactions.⁷

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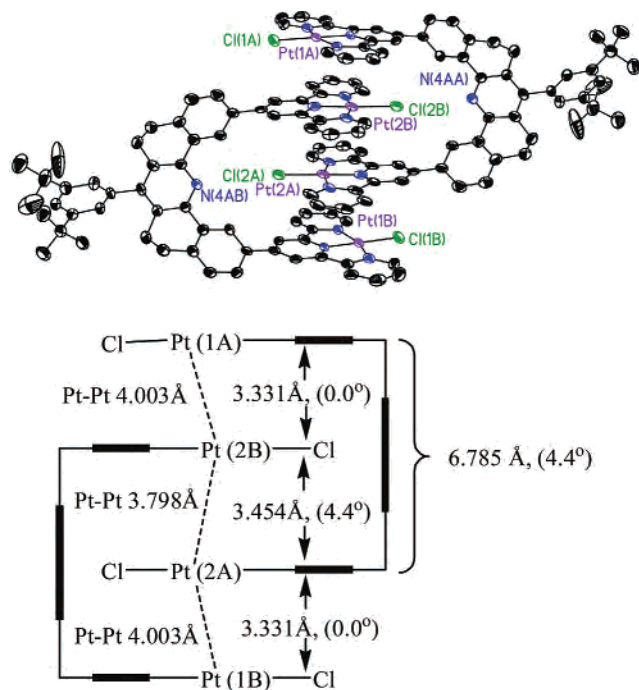


Figure 1. (Top) ORTEP diagram showing a side view of the interlocking structure that is present in the crystal of **1**-Pt²⁺-9DMF. The solvent and counterions have been removed for clarity. Hydrogen atoms were not located. Thermal ellipsoids are shown at 50% probability. (Bottom) Schematic representation of the important structural details from the crystal structure of the receptor.

Considering the molecular recognition observed for the Pd²⁺ and/or Pt²⁺ receptors with guests **2** and **3**, it is probable that π - π interactions and charge-induced dipole interactions exist in all of the host-guest adducts.⁸ For the Pt²⁺ receptor, **1**, Pt-Pt interactions in the host-guest adducts will presumably also enhance stability. The idea that weak metal-metal interactions can contribute to molecular recognition was examined as follows.

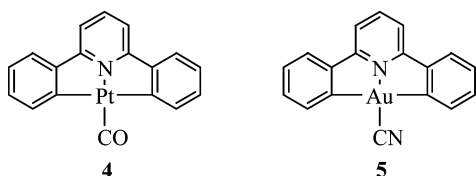


Figure 2. ORTEP diagram showing the stacking that is present in the crystal of **5**. The thermal ellipsoids are shown at the 50% probability. Difficulties were encountered in making suitable absorption corrections because of (1) the very high absorption coefficient (10.7 mm⁻¹), (2) the extreme shape of the crystal with a 5:1 aspect ratio, and (3) the lack of a complete data set allowing accurate multiscan correction using SADABS. We believe that these factors affected the thermal parameter generation.

Guest **4** was obtained by a modification of a reported procedure,¹¹ and **5** was prepared from the known chloro precursor.¹² In the solid state, an analogue of **4** exists as dimers with a Pt-Pt distance of 3.243 Å,¹³ indicating significant Pt-Pt interaction.⁷ The crystal structure of **5** is shown in Figure 2, where the planes of the planar molecules are parallel but slip-stacked. The interplanar separations are 3.385 Å, and the distance between neighboring Au³⁺ atoms is 4.901 Å, indicating the absence of significant Au-Au interaction.⁹ Other parameters are unexceptional.¹²

The stoichiometry and stability constants for host-guest formation between the Pt²⁺ receptor and **4** and **5** were determined by the ¹H NMR chemical shift titration “mole ratio” method¹⁴ in DMF-*d*₇ at 70 °C, a temperature at which rapid exchange occurs on the ¹H NMR time scale. Both systems form 1:2 host-guest adducts (Figure 3). The two stability constants were determined by curve-fitting the ¹H NMR titration data using the previously reported algorithm.¹ It was found that, for the 1:2 adduct between the Pt²⁺ receptor and **4**, the microscopic stability constants were 3500 and 450 M⁻¹. The corresponding constants for the 1:2 adduct formed between the Pt²⁺ receptor and the gold guest, **5**, were found to be 1800 and 300 M⁻¹. The reason that **4** and **5** give 1:2 host-guest adducts whereas analogous adducts with **3** give

The two potential guests **4** and **5** are isoelectronic; **4** can engage in Pt-Pt interactions with the Pt²⁺ receptor, but with **5**, such analogous interaction is unlikely to occur with the Pt²⁺ and Au³⁺ ions.⁹ Thus, assuming that **4** and **5** have similar solvation energies,¹⁰ if it is found that **4** forms a stronger adduct with the Pt²⁺ receptor than does **5**, it would be reasonable to assume that the enhanced stability is due to a Pt-Pt interaction.

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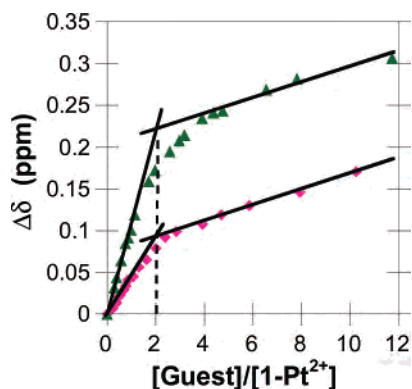


Figure 3. ^1H NMR stoichiometry titration for the host–guest complex formed between the receptor **1** (Pt^{2+}) and the potential guests **4** (\blacktriangle) and **5** (\blacklozenge). The experiments were performed at 70°C in $\text{DMF-}d_7$ with the concentration of **1** (Pt^{2+}) held constant at 1.34 mM . The concentration of **4** was varied between 0.34 and 15.70 mM , and the concentration of **5** was varied between 0.35 and 13.70 mM . The plot refers to the proton H_g (see **1**). Other proton shifts gave similar plots.

1:1 adducts might be related to the larger π -surface present in **4** and **5**. The larger constants of the **1–4** adduct compared with **1–5** are consistent with Pt–Pt interactions contributing to host–guest stability. However, we have not succeeded in growing crystals of either of these adducts that were suitable for X-ray diffraction. To infer the structures of these adducts in solution, ^1H NOE experiments¹⁵ were performed.

These experiments revealed that the two adducts exhibit different solution structures. Figure 4 shows the important intermolecular cross-peaks that were observed for the two adducts. The NOE data imply that both adducts have one guest in the molecular cleft and one occupying the outer faces of the (two) terpy–Pt–Cl units. In the **1–4** adduct, the guests lie in orientations that are the “reverse” of that inferred for the adduct formed by **1** and **5**. Whereas the two adducts are not structurally analogous, the orientation of **4** is the same as that found for the Pt–Pt interaction guest **3** and the Pt^{2+} receptor in solution and in the solid.⁴ The fact that the platinum and gold adducts have different orientations suggests that different forces operate to provide stability. The most likely difference between the two is that stabilizing Pt–Pt interactions occur in the adduct formed with the platinum guest, **4**. Molecular models (see Supporting Information) of the two host–guest adducts indicate that, in the case of the orientation adopted by the **1–4** adduct, Pt–Pt interactions can easily occur but the possible Pt–Au interactions are not readily achieved in the inferred orientation of the **1–5** adduct.

ESI-MS (DMF) indicates ions for the two adducts that represent a 1:1 host–guest adduct in both cases, and both show the expected isotopic distribution (see Supporting Information). That 1:1 adducts are observed indicates that

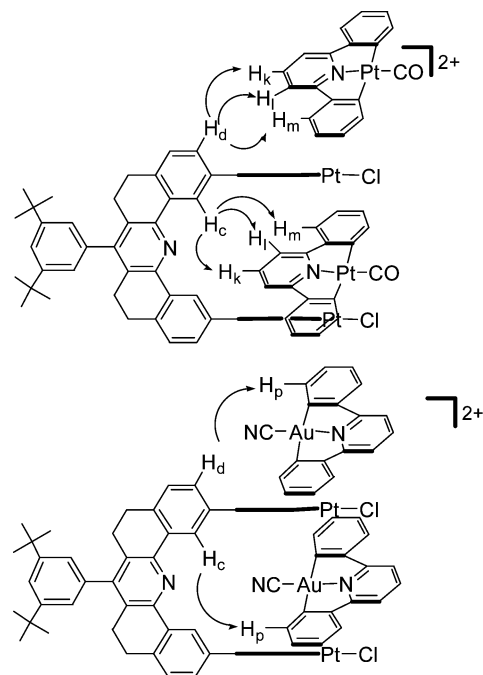


Figure 4. Observed intermolecular NOE cross-peaks for the adducts formed by the Pt receptor with **4** (top) and **5** (bottom). Because of the 2-fold symmetries of the receptor, the guest, and the adducts, only one set of symmetry-related cross-peaks is shown.

only the more stable guest is maintained in the mass spectrometer, namely, the adduct bearing the guest within the cleft.

It is interesting that the formation of host–guest adducts with either the Pd^{2+} or Pt^{2+} receptor, **1**, and guests **2–4** is signaled by the appearance of a deep red color but, for the case of the adduct formed between the Pt^{2+} receptor and the gold guest **5**, no visible color change is observed when the adduct forms (see Supporting Information for spectra).

For these host–guest systems, π – π and, in the case of the Pt^{2+} receptor and Pt^{2+} bearing guest, weak metal–metal interactions are important not only for adduct stability but also for controlling the adduct structures.

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Supporting Information Available: Experimental procedures, molecular modeling, ^1H NMR stoichiometry plots, ESI-MS, UV–vis spectra, COSY and NOESY spectra for host–guest adducts **1–4** and **1–5** and one crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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