Supramolecular Recognition: Use of Cofacially Disposed Bis-terpyridyl Square-Planar Complexes in Self-Assembly and Molecular Recognition

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In memory of *Luigi M. Venanzi*, able chemist, generous man

A molecular receptor consisting of a molecular spacer that constrains two terpyridyl-palladium(II) complexes to be disposed in a parallel cofacial geometry has been prepared. The separation between the two terpyridyl-palladium units is enforced to be *ca.* 7 Å, a distance sufficient to incarcerate aromatic molecules and square-planar complexes. A number of molecules are shown to associate with this spacer-chelator complex. In particular, 9-methylanthracene (9-MA) is found to form a 1:2 host-guest complex. A crystal structure of this complex shows one 9-MA in the molecular cleft formed by the two terpyridyl-palladium units and the other 9-MA molecule to lie above one of the terpyridyl-palladium units. Nuclear *Overhauser* effects on analogous molecules that contain two anthracene guests tethered intramolecularly indicate that the structure found in the solid is similar to that in solution. Low-temperature ^{1}H-NMR studies indicate rapid exchange between the two binding sites. The spacer-chelator complexes, when combined with appropriate molecular linkers, readily form molecular rectangles, trigonal prisms, and tetragonal prisms. One molecular rectangle is shown to associate with up to five 9-MA molecules.

Introduction. – Chemistry is in the midst of a profound transformation from the traditional areas that have been dominant for a hundred years to an era where new challenges present themselves. The reasons for this change are partly related to the maturity of the field, which allows for the construction of larger and more complicated molecules, the demands of materials science, and the inspiration provided by biology. There are many approaches to this new era of chemistry currently being pursued, one of which is entry into the mesoscopic domain by deployment of weak interactions in thermodynamically controlled self-assembly.

Hitherto, organic molecules and some inorganic molecules were constructed under kinetic control where the bonds, once formed, were stable. There are limits to this approach, however, because the construction of nanoscale molecules with specific structures becomes a formidable task under these kinetically controlled methods. One way around this problem is to encode in the kinetically stable parts of the supramolecule the information necessary for the constituent parts to self-assemble under thermodynamic control. This approach to the mesoscopic molecular scale requires understanding of the factors that will guide the constituent parts to spontaneously self-assemble.

Once self-assembled, the supramolecules can display various properties that rely on molecular recognition. Supramolecular recognition is controlled by the structure of the host and by the weak, usually noncovalent, interactions that exist in the host-guest complex. The other challenge in supramolecular chemistry, therefore, is to understand how to deploy these weak forces in recognition and in site-selection within the host.

This short review describes some of our work in trying to understand supramolecular self-assembly and molecular recognition with transition metal complexes. Before this is presented, it is useful to outline the forces that control self-assembly and molecular recognition.

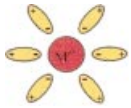
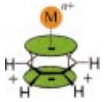
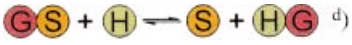
Self-Assembly and Molecular Recognition Interactions. – *Table 1* lists three types of bonds that can be used to form supramolecular structures. Included are the range of bond strengths, their thermodynamic stability, and their kinetic lability. The energies of the bonds span wide ranges, and there are examples of bond energies that fall outside of these ranges within each category, but the ranges given serve as an approximate indication of bond strength. Both H-bonds and weak coordinate bonds can be used for molecular recognition as well as for assembly. As noted earlier, covalent C-bonds are generally nonlabile, and, hence, self-assembly driven by these bonds is usually precluded. This also is generally the case for third-row transition metal bonds, although bond lability depends on the ligand and metal and on the presence of labilizing effects, such as the *trans*-effect. First- and second-row transition metal bonds are generally sufficiently labile for self-assembly, although there are exceptions in these cases also that depend on the metal, the ligand, and the labilizing effects of other ligands. H-Bonds are of medium stability but of high lability: several of these bonds are generally required for self-assembly and usually require the absence of a noncompeting H-bonding solvent. The overall conclusion is that self-assembly is most likely to occur with first- and second-row transition metals and with multiple H-bonds. There are numerous examples of supramolecular assemblies formed with coordinate bonds [1] and a number of elegant studies by *Rebek* on H-bond assemblies [2].

Table 1. *Supramolecular-Assembly Bonds*

Interactions	Energy (kcal/mole)	Stability	Lability	Illustration
Covalent Carbon Bond	40–120	High	Low	C–Y
Covalent	20– 80	High	High	1st Row M–L
Coordinate		High	Medium	2nd Row M–L
Bond		High	Low	3rd Row M–L
H-Bond	1– 15	Medium	High	A–H···:B

Table 2 lists types of supramolecular-recognition interactions. The approximate energy range of each interaction is provided, the distance dependence of the interaction is given, and, although the stabilities of the interactions vary greatly, all of the interactions lead to kinetically labile associations. The distance dependence of the interactions varies from $1/r$ to $1/r^6$. The distance dependence of cation-π and π-π stacking interactions depends on how these interactions are treated. Noncovalent cation-π interactions are assumed to arise from charge-dipole and from charge-induced-dipole interactions. The π-π stacking interactions are assumed to be controlled by dipole-dipole and by dispersion interactions. For any host-guest complex, it is not always possible to identify a single dominant interaction, and association can arise from a combination of interactions. Aside from ion-ion interactions, the rapidly attenuating

Table 2. *Supramolecular-Recognition Interactions*

Interactions	Energy (kcal/mole)	Distance Dependence	Stability	Lability	Illustration
Ion-ion	10–90	$1/r$	High	High	
Ion-dipole	10–50	$1/r^2$, $1/r^4$ [a])	High	High	
Dipole-dipole	1–10	$1/r^3$, $1/r^6$ [a])	Low	High	
Cation-π [b])	1–20	$1/r^2$, $1/r^4$ [b])	Medium	High	
π-π-Stacking [c])	1– 5	$1/r^3$, $1/r^6$ [c])	Low	High	
Dispersion	1– 5	$1/r^6$	Low	High	
Solvent effects	1–10		High	High	 [d])

[a]) The inverse distance dependence is different for a fixed ion-dipole ($1/r^2$) compared to a freely rotation ion-dipole interaction ($1/r^4$). For dipole-dipole interactions, fixed dipoles have a $1/r^3$ distance dependence whereas freely rotating dipoles vary as $1/r^6$. [b]) Non-covalent cation-π interactions are assumed to be controlled by charge-dipole interactions ($1/r^2$) and by charge-induced dipole interactions ($1/r^4$). [c]) π-π Interactions are assumed to be controlled by fixed dipole-dipole interactions ($1/r^3$), by freely rotating dipole-dipole interactions ($1/r^6$), and by dispersion interactions ($1/r^6$). [d]) S = solvent, G = guest, H = host.

distance dependence of the interactions indicates that molecular recognition is a subtle phenomenon that depends critically on the dimensions of the receptor site and those of the guest and, in the case of dipolar interactions, on favorable host-guest orientation. Despite the subtleties of the interactions, there are examples of ion-ion [3], ion-dipole [4], dipole-dipole [5], cation-π [6], π-π stacking [7], and dispersion [8] interactions that lead to molecular recognition of guests by receptor molecules. In all of these cases, the receptor cavity and the guest dimensions are such as to allow for the major interactions to operate. Guest incarceration depends also on the solvent in which the experiment is done. Thus, for example, a hydrophobic guest in H_2O will transfer to a receptor with a hydrophobic cavity more readily than if the experiment is conducted in hydrocarbon solvents. This effect can be large and decisive and has been demonstrated in many cases [9].

The illustrations in *Table 2* are largely self-explanatory, but the π-π stacking pictures deserve comment. On the assumption that these interactions are mainly

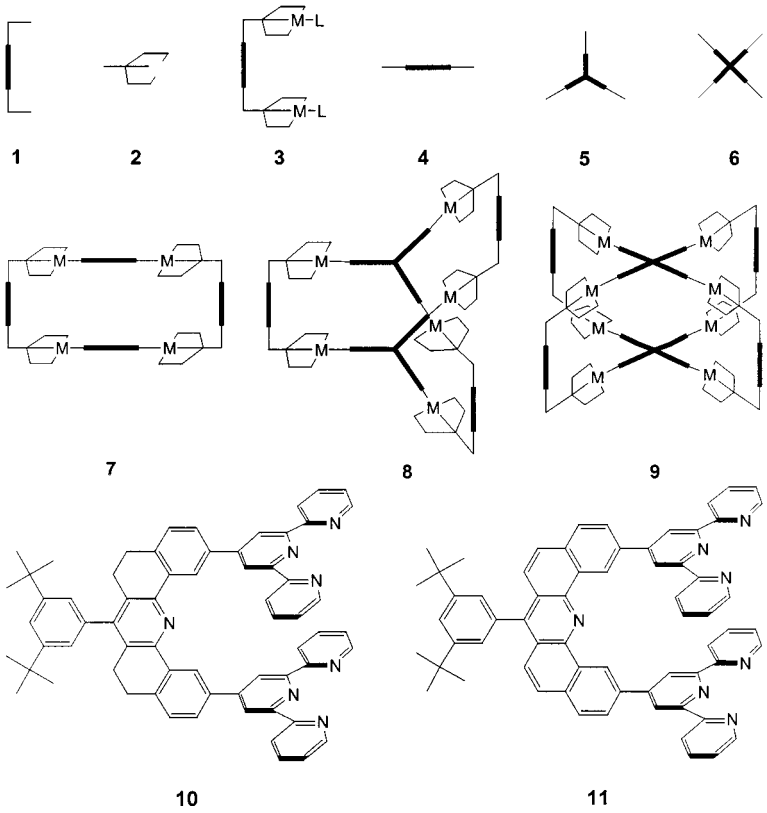
controlled by dipolar interactions [10], the orientation of two benzene molecules is most favorable in the T disposition (right), which is followed by the slipped parallel structure (middle), and the least favorable is an eclipsed structure (left). The π-π stacking interactions and the dispersion (*London*) interactions tend to increase with the size of the interacting molecules.

We now describe some of our work on self-assembly and molecular recognition with square planar palladium(II) complexes.

Construction of Supramolecular Receptors. – Most self-assembled supramolecules incorporating square-planar complexes thus far reported have used the two *cis*-disposed ligand binding sites to elaborate into the supramolecular domain with large linker organic ligands [1]. These systems have provided a remarkable number of complex structures, many of which have been shown to incorporate one or several guest molecules. Our approach is somewhat different in that two square-planar metal complexes are held cofacially at a fixed distance, and the supramolecules are elaborated from this structure.

The supramolecular assemblies are constructed from a number of elements. These elements consist of a spacer **1**, a planar tridentate chelator **2**, a spacer-chelator complex **3**, and a variety of linkers **4**, **5**, and **6**. With the spacer-chelator complex **3** when L is a good leaving group, the addition of the linkers, **4**, **5**, and **6** should provide the molecular rectangle **7**, the molecular trigonal prism **8**, and the tetragonal prism **9**. It is probable that the formation of **7**, **8**, and **9**, is facilitated by minimizing the number of molecular degrees of freedom of the constituent parts. Thus, rigid spacer-chelator complexes and rigid linkers are more likely to form the supramolecular structures, **7**, **8**, and **9** than when these elements are flexible. Our initial work on spacer-chelator complexes indicates that the chelators are required to be rigidly held in cofacial dispositions in order to obtain the supramolecular structures in high yield. Some flexibility in the spacer-chelator complexes is desirable, however, for molecular recognition. In particular, free rotation of the chelators attached to the spacers is useful in adjusting the interplanar chelator complex separations, which depend on the dihedral angle between the mean molecular planes of the spacer and chelator. This interplanar separation flexibility allows for maximum interaction between the host and guest. To incorporate an aromatic molecule or a square planar metal complex between the two parallel chelator complexes, a separation of *ca.* 7 Å is required [11][12]. To avoid stereochemical ambiguity, the tridentate chelator is required to be symmetrical and planar. Within these restrictions, the charge of the spacer-chelator complexes can be varied from positive to neutral to negative. Such charge variation extends the range of molecular recognition that can occur according to the charge and dipolar demands of the guest.

After consideration of these requirements, the first set of spacer-chelators was prepared, **10** and **11**, which differ from each other by having reduced spacer rings and fully oxidized spacer-ring systems, respectively. The presence of the two *t*-Bu groups in these spacer-chelators is crucial in obtaining solubility in common organic solvents. The spacers of **10** and **11** are the same as those used by *Zimmerman et al.* [13] for his molecular tweezers. The preparation of **10** and **11** by conventional methods was tedious but provided gram quantities of the spacer-chelators [14].

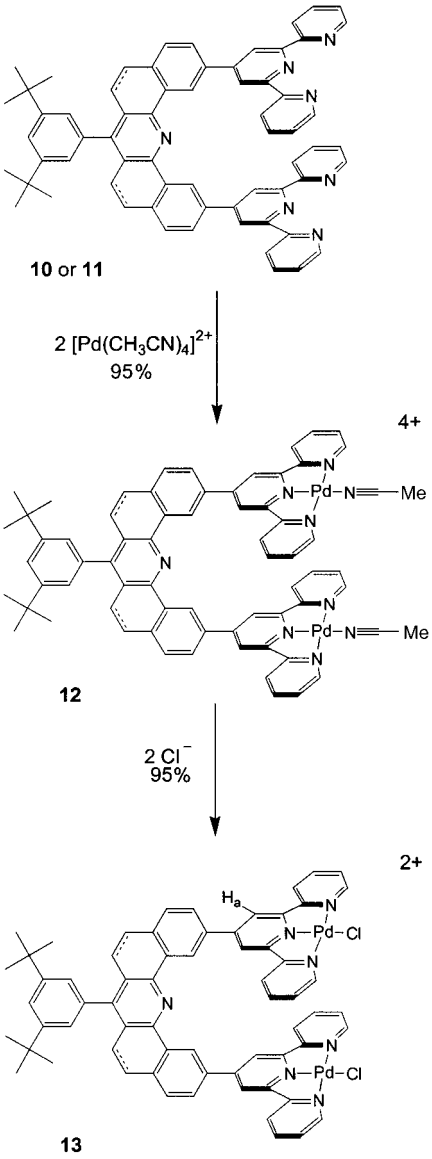


Preparation of Spacer-Chelator Complexes. – Given the length of the organic synthesis of the two spacer-chelators and the presence of two chelators in the same molecule, it was important to devise efficient methods for the preparation of their complexes. Terpyridyl (terpy) complexes of Pd^{2+} and Pt^{2+} are usually prepared in moderate yield from their chloro complexes. For Pd^{2+} complexes, we found [14] that using the $[Pd(MeCN)_4](PF_6)_2$ complex as the source of Pd^{2+} gave the MeCN complex **12**, and, thereafter, the chloro complex **13**, in essentially quantitative yields. The sequence is shown in *Scheme 1*.

As expected, the MeCN ligands of **12** are readily substituted, whereas the chloro ligands of **13** are less labile. Thus, the complexes **12** were used for the synthesis of supramolecular assemblies. These will be discussed presently, but first we describe the molecular recognition displayed by the reduced complex **13**. Molecular models indicate that the metal-metal separations in **13** are *ca.* 7 Å. As noted, this value can vary according to changes in the interplanar angles between the spacer and the terpyridyl-Pd-L units.

Molecular Recognition. – Molecular recognition studies were carried out principally with the reduced spacer **13** in MeCN solutions. *Fig. 1* depicts some of the potential guests that have been investigated.

Scheme 1



Strong binding occurs with 9-methlyanthracene (9-MA), 9-methyl-9*H*-carbazole and 2,2′-bi-1,3-dithiolylidene. When the first two are added to a yellow solution of **13**, a bright red color appears, and the last gives a green solution. The bis-8-hydroxyquinolato Pd^{2+} complex also forms a strong complex. Weak binding is observed with several aromatic molecules and with the Rh^{+} dicarbonyl complex. As we discuss shortly, the extent of binding can be estimated by chemical-shift titrations. The ^{1}H-NMR spectra

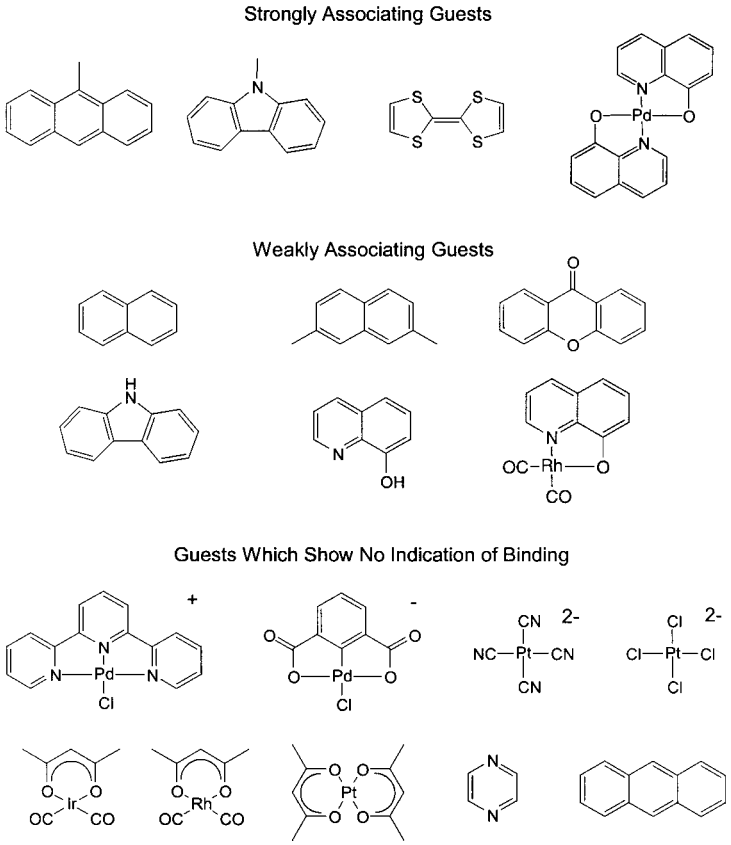


Fig. 1. *Some guest molecules that were investigated for molecular recognition by the reduced receptor* **13**

show shifts in both the host and the guest upon association. The bottom segment of *Fig. 1* shows a series of molecules that showed no association in MeCN solutions. The positively charged complex, $[Pd(terpy)Cl]^+$, which would be expected to fit well within the molecular cleft, shows no association because of the positively charged host and guest. The negatively charged complexes would be expected to associate because of charge attraction, but each was found to give intractable precipitates with the potential host. Were this insolubility overcome, we would expect these negatively charged guests to form strong host-guest complexes because of ion-ion attraction. Curiously, none of the acetylacetonate complexes associated with the receptor: the reasons for this are unclear. The pyrazine molecule does not incarcerate by forming internal axial bonds to the two Pd-atoms of the receptor. Anthracene, like 9-MA, was expected to form an association complex but is prevented from doing so by its insolubility in MeCN. These results illustrate some of the factors that influence whether or not **13** forms associations. When the association complexes are soluble, it appears that large aromatic guests form the strongest complexes. The forces which control the degree of association appear to be subtle, however. We present two studies of host-guest association, one

involving the bis-8-hydroxyquinolato-Pd^{2+} ($[Pd(OQ)_2]$) complex and the other with 9-MA.

Fig. 2 shows the spectral changes that occur when $[Pd(OQ)_2]$ associates with **13** in MeCN solutions. The spectra shown are those of $[Pd(OQ)_2]$ (*Fig. 2,b*), **13** (*Fig. 2,a*), a normalized sum of these two spectra (*Fig. 2,d*) and the spectrum of the host-guest complex (*Fig. 2,c*). It is clear that the host-guest complex gives a distinct spectrum that is not the normalized sum of the constituent parts. Such new spectral features observed upon host-guest association are usually referred to as 'charge-transfer' bands, presumably to imply electronic excitation between the host and guest. We have no evidence to either support or discount this assumption, but we note that the new bands could arise from energy shifts of existing transitions caused by association. The stability of the host-guest complex could result from π-π-stacking interactions and from metal-metal interactions between the Pd atoms of the host and guest [12]. We have been unable to determine the stability constant of host-guest association because of the insolubility of $[Pd(OQ)_2]$ in MeCN solutions, but we believe that the stability is high. Addition of (solid) $[Pd(OQ)_2]$ to solutions of **13** at *ca.* 50° leads to the slow dissolution of the $[Pd(OQ)_2]$ complex until one equivalent is added. Thereafter, no dissolution of $[Pd(OQ)_2]$ occurs. This indicates that a 1:1 host-guest complex forms and that its stability is greater than the stability of the $[Pd(OQ)_2]$ crystal.

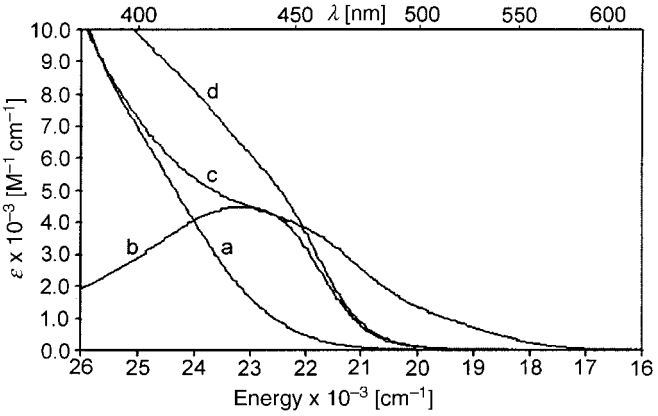


Fig. 2. *Absorption spectra for* a) **13** *$(PF_6)_2$* (2.74 mM), b) *$Pd(OQ)_2$* (2.74 mM), c) *1:1 solution of* **13** *$(PF_6)_2$ and $Pd(OQ)_2$* (2.74 mM each), *and* d) *the normalized sum of* a) *and* b)

Because 9-MA is conveniently soluble in MeCN solutions, it was possible to do a more complete study of its binding to the reduced receptor, **13**. *Fig. 3* shows the absorption spectra of the host, the guest, and the host-guest association complex. A well-resolved absorption band at *ca.* 20000 cm^1 is observed for the host-guest adduct. The electronic provenance of this transition(s) has not been determined. As noted before, it could be a host-guest charge-transfer band, or it could arise from modification of existing transitions.

When 9-MA is added to solutions of the receptor, the ^{1}H-NMR spectra show displacements of the chemical shifts of some of the protons of the host and of the guest. A plot of these chemical-shift changes ($\Delta\delta$) *vs.* the ratio of 9-MA to **13** gives plots that

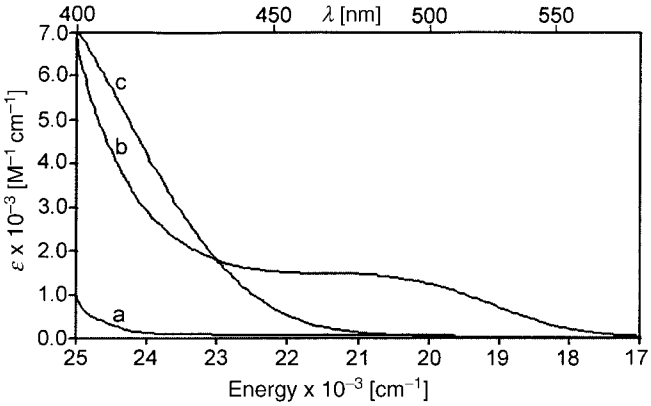


Fig. 3. *Absorption spectra for* a) *9-MA* (50.0 mM), b) *9-MA* (50.0 mM) *and* **13** *$(PF_6)_2$* (5.00 mM), *and* c) **13** *$(PF_6)_2$* (5.00 mM)

indicate the stoichiometry of adduct formation and from which the stability constants of association can be estimated. An example [14] of such a plot is given in *Fig. 4*. The ^{1}H-NMR spectra at 23° indicate that the 9-MA guest engages in rapid exchange with the host. The plot establishes that a 1:2 host-guest adduct is formed, and the stability constants are estimated to be 650 M^{-1} and 200 M^{-1}. That a 1:2 adduct is formed is surprising, and, although we would expect one of the 9-MA guests to occupy the cleft, it is not clear how to assign the residency of the other. This question is resolved to some extent by a crystal structure of the host-guest complex and by other experiments that are described later.

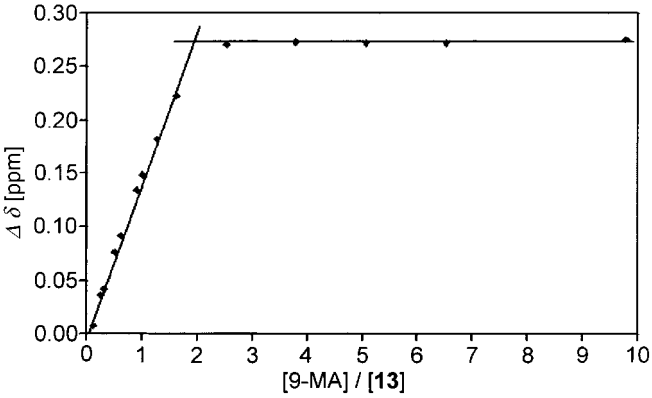


Fig. 4. *A plot of the ^{1}H-NMR chemical-shift changes for protons H_a (Scheme 1)* vs. *the ratio of [9-MA] to [***13***]*. The experiments were performed in CD_3CN at 23° with the concentration of **13** $(PF_6)_2$ constant at 5.00 mM and the concentration of 9-MA varied between 0.5 mM and 50 mM.

Crystal Structure. – The crystal structure of the 1:2 host-guest complex was determined, and three perspectives of the structural units are illustrated in *Fig. 5*. One 9-MA molecule resides in the molecular cleft but the other lies outside of the cleft. The spacer chelator exists in a racemic configuration, and, although the terpy-Pd-Cl units are

parallel, the spacer is twisted from being perpendicular to these planes. This twisting of the spacer allows the interplanar separation between the two terpy-Pd-Cl units to be 6.92 Å rather than about 7.1 Å if the spacer and terpy-Pd-Cl planes were perpendicular. This cleft contraction allows for an ideal fit for the 'thickness' of the 9-MA molecule which is 3.46 Å. It appears, therefore, that the interplanar separations between the host and guest in the cleft have been optimized for maximum stability. The forces that stabilize the guest in the cleft are probably π-π stacking attractions and possibly charge-induced dipole attractions emanating from the positive charge of the terpy-Pd-Cl units and the negative π-clouds of the 9-MA. If this is the case, the steep distance dependence (*Table 2*) of these forces requires that the interplanar separations be close to the ideal distances. The ability of the present receptor to adjust the interplanar terpy-Pd-Cl separation may, therefore, be a crucial feature that leads to guest-host stability.

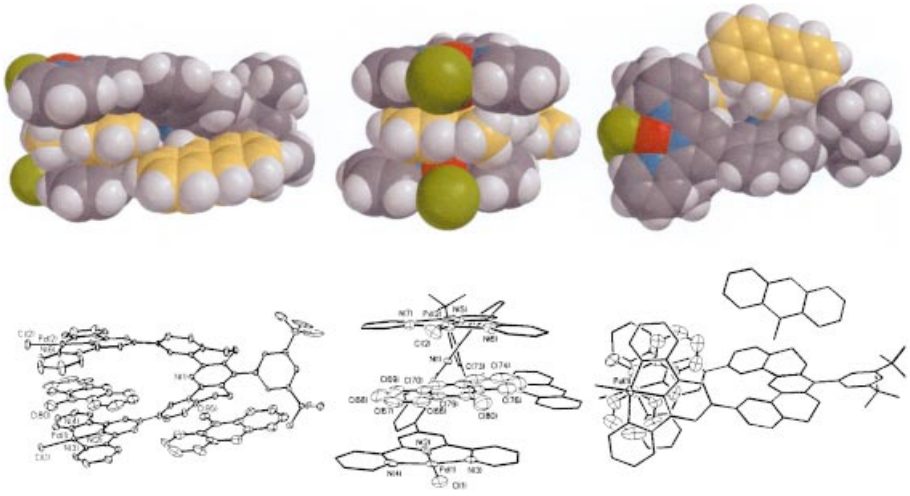


Fig. 5. *Three perspective views of the molecular adduct [***13***(9-MA)]$^{2+}$ · 9-MA.* Bottom row (left to right): a 'side' view thermal ellipsoids at 25% probability, and 'front' and 'top' views, where the incarcerated 9-MA is shown as thermal ellipsoids in all cases. The top row shows these structures as space-filling models with H-atoms included (H, white; Pd, red; Cl, green; receptor C, gray-black; 9-MA C-atoms are shown in yellow for clarity).

The reasons for the presence of one 9-MA molecule outside of the cleft become apparent when the overall crystal structure is considered. An illustration of the extended structure is provided in *Fig. 6*. The extended structure shows stacking of eight π-units. The 9-MA guests exist in two sites, inside of the cleft and outside the cleft interacting with the outside face of one of the terpy-Pd-Cl units. In addition, two terpy-Pd-Cl units of different receptors are cofacially disposed to each other. The stacking of the 9-MA guest outside of the cleft is probably the reason that this extra 9-MA molecule appears in the crystal.

Intramolecular Host-Guest Association. – The discovery of a 1:2 host-guest association both in solution and in the solid state suggested that 1:2 and 1:1 associations could be designed into the receptor by intramolecular association. This idea is illustrated by the two complexes, **14** and **15**, that have been prepared. Both of these

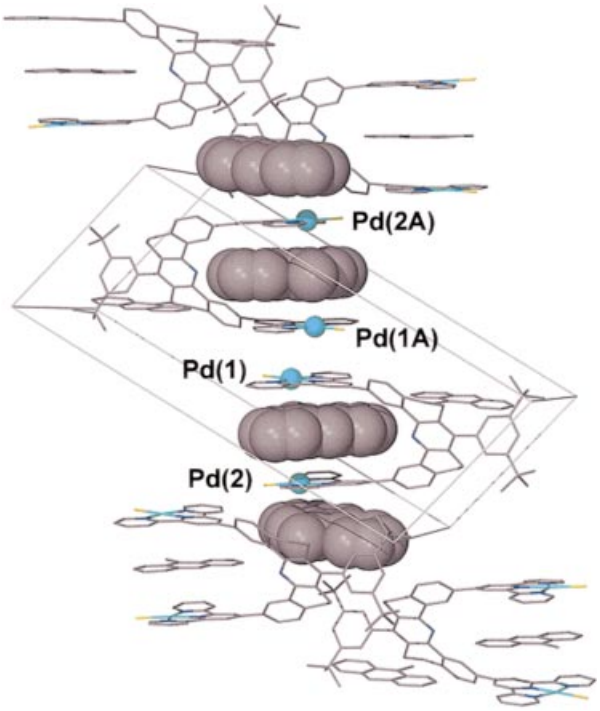
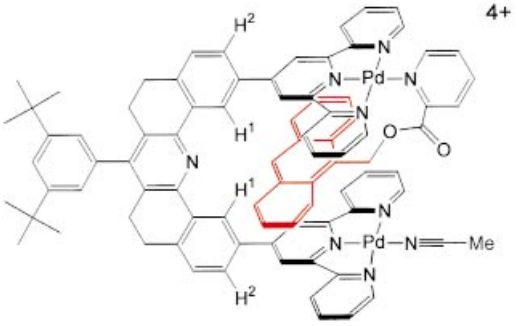


Fig. 6. *An illustration of the extended structure of [**13**(9-MA)]$^{2+}$ · 9-MA.* The box is the unit cell; 9-MA molecules of the stack are shown as space-filling models and the terpy-Pd-Cl units are shown as stick models, as are all other molecules not involved in this stack. Pd-Atoms in the stack are shown as blue spheres

molecules show electronic spectral changes, compared to the mono- and bis-pyridine analogues, indicative of anthracene guest incorporation. The ^{1}H-NMR spectrum of **15** at 20° in acetone solution is that of a symmetric complex. When these solutions are incrementally cooled to −90°, some of the ^{1}H-NMR signals first broaden and then separate into two sharp signals of equal intensity at −90°. At this temperature, distinct signals for the two anthracene protons are observed and the proton signals of the receptor reflect an unsymmetrical molecule. No such changes are observed for **14** under the same conditions. Rotating-frame *Overhauser* enhancement spectroscopy (ROESY) performed on **14** and **15** at 20° in acetone solution reveal enhancements that are indicative of the solution structures. Adduct **14** shows *Overhauser* enhancements of the H^1 protons of the spacer but **15** shows enhancements of both the H^1 and H^2 protons. In both cases, enhancements are observed for the protons at C(4), C(5), and C(10) of the anthracene. At 20°, both of the H^2 protons of **15** are enhanced, indicating that, on the ^{1}H-NMR time scale, both outside sites of the two terpy-Pd-Cl units are populated by anthracene. This latter observation is consistent with the temperature-dependent behavior of **15**.

The ^{1}H-NMR results for **15** are consistent with the dynamic fluxional process shown in *Scheme 2*. The complexes **16** and **18** are identical but serve to illustrate how the two H^2 protons become equivalent. The putative symmetrical intermediate **17** is not



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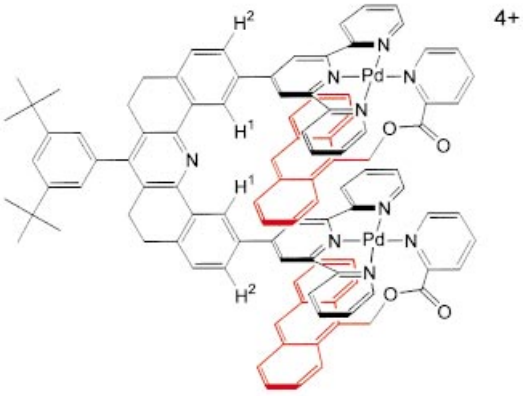


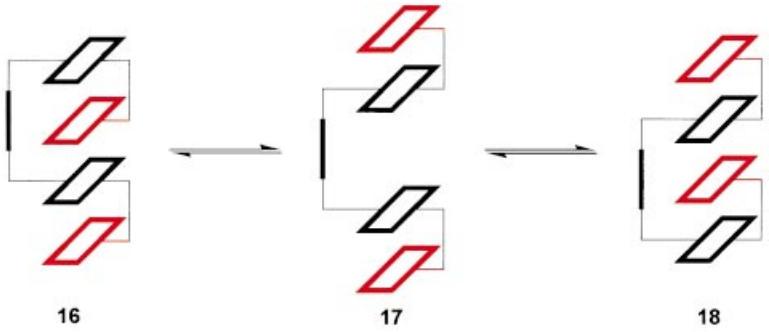
15

observed, but an intermediate resembling **17** is required in order for site exchange to occur. The dynamic process **16** ⇌ **18** was found to have a *Gibbs* energy of activation of *ca.* 10 kcal/mole, indicating a very rapid site-interchange process. The adduct **14** is probably also in dynamic exchange with the outer site, but this process is not observed because of the strong thermodynamic preference of the anthracene to occupy the cleft. This assertion is supported by the stability constants measured for **13** and 9-MA.

The ^{1}H-NMR studies and the crystal structure support the hypothesis that the 1:2 host-guest adduct formed by **13** and 9-MA consists of one 9-MA in the cleft and the other residing above one of the terpy-Pd-Cl units of the receptor, a structure that **15** possesses.

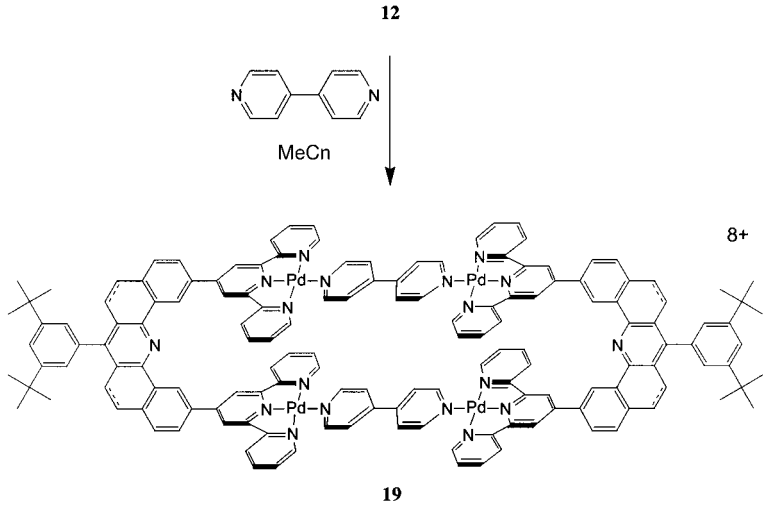
Molecular Rectangles and their Guests. – Molecular rectangles **19** are formed by the addition of either the reduced or oxidized spacer of **12** to the linear linker 4,4′-dipyridyl (*Scheme 3*) [14]. In MeCN solutions at 20° these rectangles are formed quantitatively within a few minutes. Their ^{1}H-NMR spectra and ESI mass spectra are consistent with the proposed structures. The ^{1}H-NMR spectra indicate free rotation of

Scheme 2



the 4,4′-dipyridyl ligand and the possible conformational isomers that could exist when the reduced spacer forms the rectangle appear to be in rapid interconversion because the spectrum indicates a symmetrical D_{2h} structure.

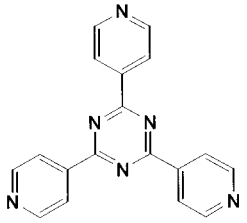
Scheme 3



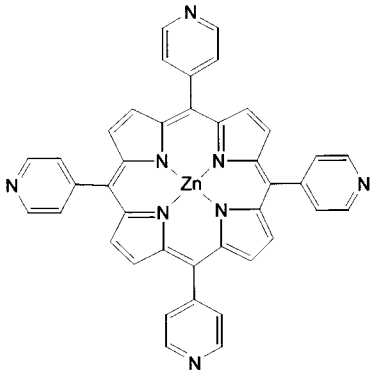
In MeCN solution, both rectangles form multiple adducts with 9-MA [15]. Plots of the kind shown in *Fig. 4* show that the reduced rectangular receptor accepts four 9-MA guests, and that the oxidized spacer accepts five 9-MA guests. The preceding studies on guest association suggest that, in the case of the reduced spacer rectangle, two of the 9-MA are in the two terpy-Pd-Cl formed clefts, and that the other two 9-MA guest lie above terpy-Pd-Cl units of different spacer-chelator units. A similar association of four of the 9-MA guests is probably obtained for the oxidized rectangle; the fifth 9-MA may reside between the two 4,4′-bipyridyl linkers of the rectangle. It is not obvious why the two rectangles should have different levels of association, but the observation does indicate that molecular recognition is a subtle phenomenon. As in the previous host-

guest complexes, the 9-MA guests of the rectangles engage in rapid site exchange, since the ^{1}H-NMR spectra at 20° show only one set of resonances for 9-MA.

Molecular Trigonal and Tetragonal Prisms. – Ongoing work on trigonal prisms and tetragonal prisms is briefly described to demonstrate the rapid and efficient way in which the present spacer-chelator complexes can form large complex structures. The two linkers **20** and **21** were expected to form trigonal and tetragonal prisms, respectively. Both of these linkers are insoluble in most solvents, and DMF was used as the solvent for self-assembly. From the reduced receptor **12** and stoichiometric amounts of **20** and **21**, the trigonal prism **8** and the tetragonal prism **9** are formed rapidly and quantitatively as determined by ^{1}H-NMR spectroscopy. The rate of formation appears to be impeded only by the rate of dissolution of the insoluble linkers. Both supramolecular assemblies can be isolated in essentially quantitative yield. The rapid and clean assembly of these large structures indicates that the present spacer-chelator complexes should provide even more complex structures. It is of interest to note that the tetragonal prism incarcerates a molecule of 1,4-diazabicyclo[2.2.2]octane (DABCO), which binds internally to the two cofacially disposed zinc ions of the porphyrins [16].



20



21

Discussion. – Whereas numerous large, complex supramolecular structures based on labile metal complexes have been prepared [1–3], the present systems are different in a number of respects. The presence of a rigidly held molecular cleft is an aspect generally absent in metal-based supramolecular assemblies. Aside from generating large, complex structures, the cleft provides for the possibility of constructing large arrays through weak forces such as electrostatic and π-π-stacking interactions.

The present spacer-chelators could incorporate a variety of planar tridentate ligands, which would allow for charge variation. Thus, it may be possible to form supramolecular receptors that carry different charges at various sites. Such multiple receptors could be used for a variety of guests with different charge demands. There are other possibilities that could be exploited by the special characteristics of these spacer-chelators.

As chemistry moves from the microscopic to the mesoscopic domain, it is likely that the areas of supramolecular chemistry and molecular recognition will become ever more vigorously pursued activities. We may be *en route* from an era of kinetic to the thermodynamic control of reactions.

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