

Supramolecular Chemistry

Rare and Diverse Binding Modes Introduced through Mechanical Bonding**

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Interest in catenanes and rotaxanes has largely focused on the stimuli-induced change in the position of their components for possible exploitation in molecular devices,^[1] but other properties and features of these architectures are becoming apparent.^[2] Here, we report a previously unrecognized consequence of kinetic stabilization of an otherwise unfavorable association of molecular fragments through mechanical bonding (Figure 1). The raised energy of the interlocked components—brought about by the enforced high local concentration of convergent functional groups, the limitation in the number of conformations and co-conformations that each component can adopt, and the poor solvation of their inner surfaces—facilitates (kinetically and thermodynamically) the formation of internal and external binding motifs that are either not observed or much weaker when the same groups are not confined in this way. The effect is illustrated through a remarkable series of binding modes (including orthogonal bifurcated pyridine–pyridine hydrogen bonding,

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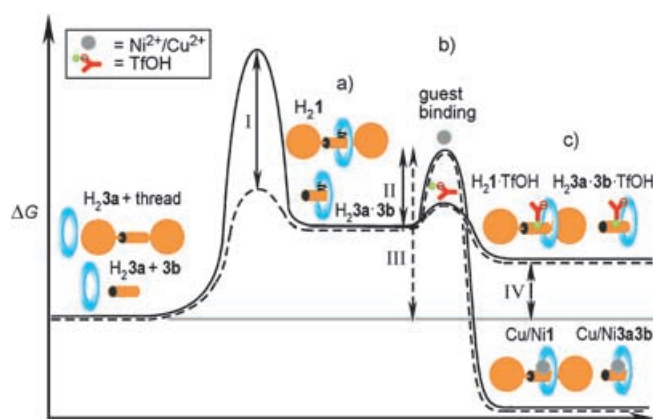


Figure 1. Effects of kinetic stabilization of an otherwise unfavorable association of molecular fragments through mechanical bonding. a) The kinetic stabilization (I) of a mechanically interlocked architecture that features only weakly attractive interactions between the macrocycle and thread permits noncovalent interactions to be observed (as in H_21) which are too weak to stabilize the corresponding host-guest complex ($H_23a \cdot 3b$). b) For a rotaxane that is not thermodynamically stable with respect to its free components, the activation energy for tertiary component complex formation is lower than for the analogous noninterlocked system (barrier II is less than III). This arises because the entropic cost of bringing the two components of the rotaxane together has already been paid, some degrees of freedom of the components are already restricted in the mechanically interlocked architecture, and the desolvation of the internal rotaxane surfaces is less energetically demanding than those of the free components. c) The higher energy of such a rotaxane means that a host-guest complex which involves the rotaxane can be favorable (e.g. $H_21 \cdot TfOH$) even when the equivalent trimolecular complex ($H_23a \cdot 3b \cdot TfOH$) is not (IV). It also ensures that metal complexes derived from such rotaxanes, such as $Cu1$ and $Ni1$, are inherently thermodynamically more stable than the analogous complexes derived from noninterlocked fragments and, in principle, kinetically easier to form. The association/dissociation pathways are shown by black solid (interlocked components) and dashed (noninterlocked components) lines; the horizontal gray line corresponds to the free energy of the nonassociated individual components.

cooperative binding to a sulfonic acid guest through deprotonation by one component and anion–amide hydrogen bonding by the other, enforced square-pyramidal coordination of Cu^{II} and Ni^{II} , and second-sphere coordination in a square-planar $Pd^{II}Cl$ complex) exhibited in solution and the solid state by a [2]rotaxane and an analogous [2]catenane, but not seen with either threadable (but nonmechanically interlocked) versions of the components or flexible covalently bonded systems (Figure 2).

Most catenanes and rotaxanes are synthesized by utilizing templates to thermodynamically favor interlocking,^[1a] but subsequent removal of the template can leave a molecule that is energetically unstable with respect to the noninter-

locked components and is only held intact by virtue of the mechanical bond. We recently described^[3] the assembly of a mechanically interlocked architecture about a Pd^{II} template to give a square-planar [2]rotaxane–metal coordination complex, $Pd1$.^[4] We were intrigued to find that upon protic demetalation of the complex to give H_21 , the 1H NMR spectrum in $CDCl_3$ indicated significant intercomponent hydrogen bonding between the amide groups of the macrocycle and the pyridine nitrogen atom of the rotaxane thread (the protons of the amide groups in the macrocycle appear 1.7 ppm downfield relative to the corresponding protons in the free macrocycle). Such a binding motif, which requires essentially orthogonal pyridine rings with the nitrogen atoms bridged by bifurcated hydrogen bonds, is extremely rare (a search of the Cambridge Crystallographic Database reveals only one other example^[5]) but is somewhat reminiscent of the hydrogen bonding that occurs at 90° to the plane of the lone pairs of amide groups in threads seen extensively in other hydrogen-bonded rotaxanes.^[6] Slow cooling of a hot, saturated solution of H_21 in acetonitrile/chloroform (10:1) yielded single crystals that were of sufficient quality to confirm the interaction in the solid state by X-ray crystallography (Figure 3a,b) but were inadequate to confidently characterize the interaction in detail.^[7] However, when we prepared a [2]catenane that incorporated the same functional groups, H_22 , a similar noncovalent interaction was observed in solution in $CDCl_3$ and, in this case, single crystals of excellent quality were obtained by slow cooling of a hot, saturated solution of H_22 in acetonitrile. The solid-state structure of H_22 (Figure 3c) closely mirrors the hydrogen-bonding motif seen in the crystal structure of H_21 , with unsymmetrical intercomponent hydrogen-bond distances (2.28 and 3.10 Å in H_22 ; 2.3 and 2.8 Å in H_21) and the angle between the planes of the

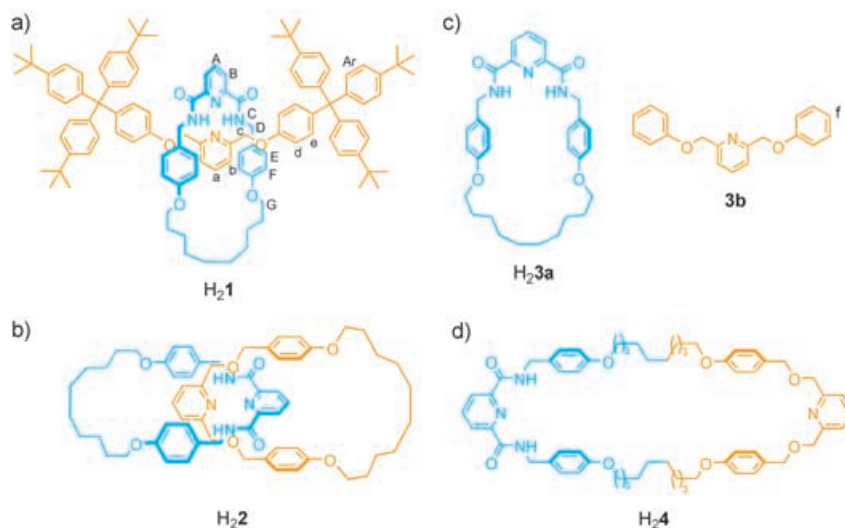


Figure 2. Different ways of linking a 2,6-dialkylpyridine unit with a 2,6-dicarboxamidepyridine unit which lead to significantly different noncovalent binding properties: a) on different components within a [2]rotaxane architecture, H_21 ; b) on different components within a [2]catenane architecture, H_22 ; c) on separate threadable, but not mechanically interlocked, molecular components H_23a and $3b$; and d) on a flexible but wholly covalently bonded system, H_24 . For 1H NMR spectroscopic assignments (see Figure 4), hydrogen atoms have been labeled A–G and a–f/Ar for the macrocycle and thread, respectively.

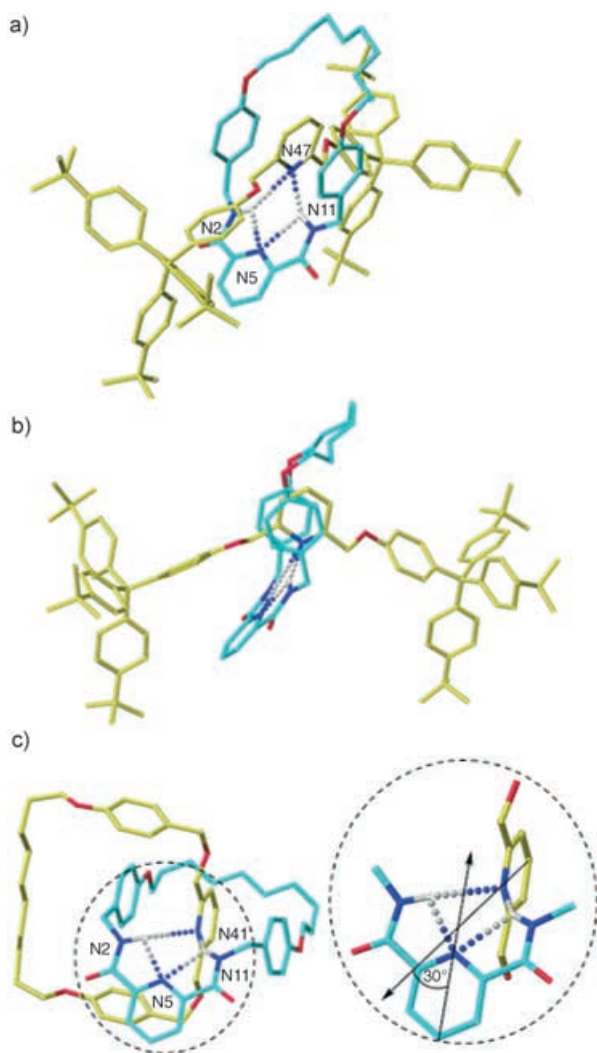


Figure 3. X-ray crystal structures^[7] of [2]rotaxane **H₂1** and [2]catenane **H₂2**: a) **H₂1** (twisted view); b) **H₂1** (side view which shows the macrocycle circumscribing the pyridine residue of the thread; disorder in the alkyl chain region and solvent molecules, not the central hydrogen-bonding region, results in a high overall *R* factor of 33 %); c) **H₂2** (*R* factor < 5 %; the intercomponent hydrogen-bond motif mirrors that shown in (a) and (b)). Inset: the lone pairs of the pyridine nitrogen atoms do not point directly at each other, but are tilted 30.0° apart. C (macrocycle) turquoise; C (thread) yellow; O red; N dark blue; H white. For clarity only nitrogen-bound hydrogen atoms are shown. Selected bond lengths [Å] for **H₂1**: N2H–N5 2.4; N11H–N5 2.6; N2H–N47 2.8; N11H–N47 2.3. Selected bond angles [°] for **H₂1**: N2H–N5 151; N11H–N5 153; N2H–N47 96; N11H–N47 108. Selected bond lengths [Å] for **H₂2**: N2H–N5 2.18; N11H–N5 2.33; N2H–N41 2.28; N11H–N41 3.10. Selected bond angles [°] for **H₂2**: N2H–N5 107.1; N11H–N5 102.2; N2H–N41 146.5; N11H–N41 129.0.

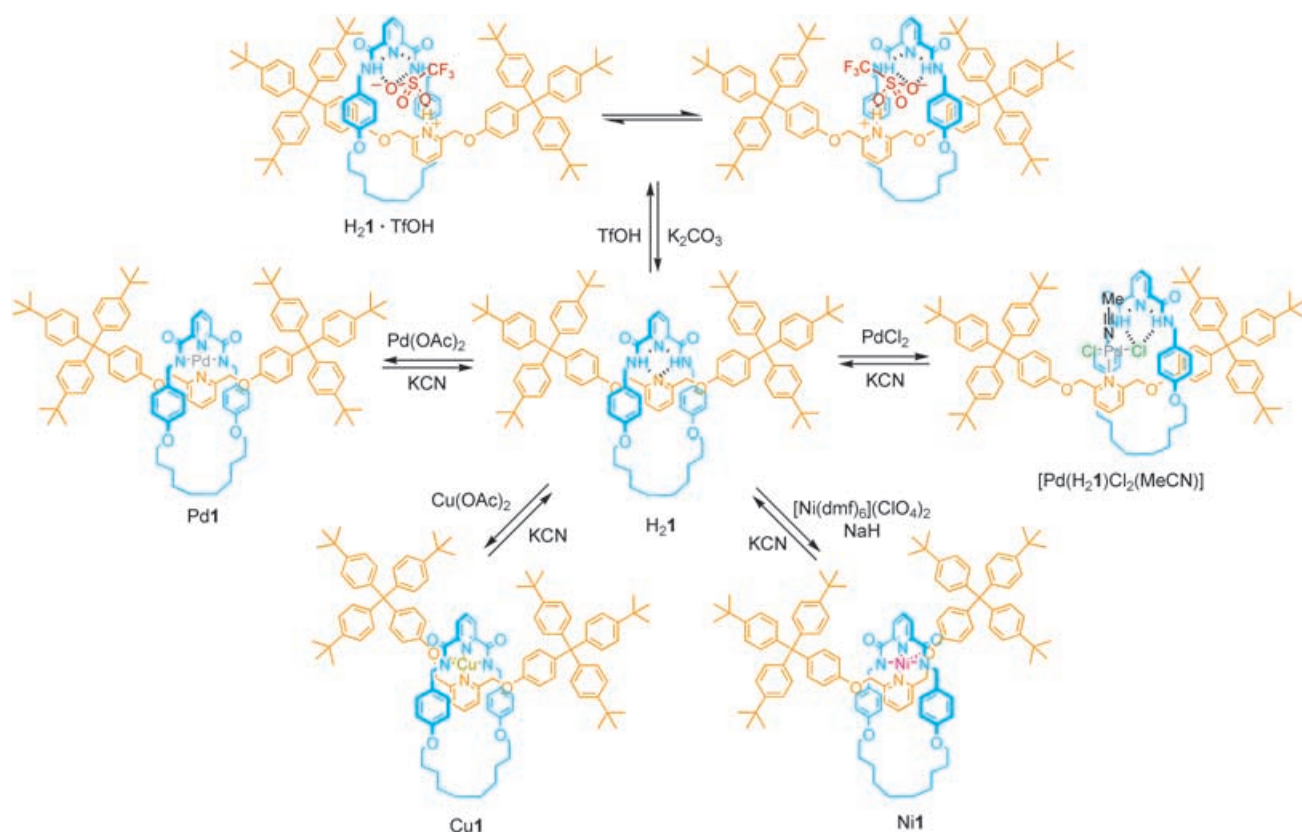
pyridine rings nearly orthogonal (90.7° in **H₂2**; 82° in **H₂1**) but tilted (30.0° in **H₂2** (Figure 3c, inset); 34° in **H₂1**) away from linearity to avoid too close an interaction between the lone pairs on the pyridine nitrogen atoms.

To investigate this atypical binding motif further, we titrated an unstopped analogue of the thread, **3b**, with the free macrocycle, **H₂3a**, and monitored the titration by ¹H NMR spectroscopy (CDCl₃) to determine the energetics

of the interaction in the absence of the kinetic barrier to dissociation provided by the mechanical bond. However, there was virtually no shift in the amide protons of **H₂3a** in the presence of up to 20 equivalents of **3b** (4–80 mM) which indicates that the bimolecular association constant must be less than 5 M^{−1}—the approximate limit of this detection method with the large shifts typically observed through hydrogen-bonding amide groups. Interestingly, the ¹H NMR spectrum of the wholly covalently linked analogue **H₂4** in CDCl₃ also gave no indication of hydrogen-bonding interactions between the pyridine-2,6-carboxamide protons and the second pyridine residue, even though this very large macrocycle is certainly flexible enough to adopt such a geometry without steric hindrance.

Rare hydrogen-bond motifs have previously been observed within rotaxane architectures (e.g. amide NH to ester acyl oxygen atoms,^[8,9] and amide NH to ester alkyl oxygen atoms^[9]). The propensity for such unusual interactions in mechanically bonded structures presumably arises for a number of reasons: 1) the enforced high local concentration of functional groups for which there is a low steric cost to relative movement within the vector of the thread; 2) the limited number of conformations and co-conformations that each component can adopt that do not put functional groups into convergent orientations; 3) the imposed orthogonalization of components which can preclude normally preferred noncovalent bonding geometries; 4) freezing out of a single co-conformation for an intercomponent binding event only costs a reduction of two degrees of freedom (translation and rotation of the macrocycle about the thread) in contrast to the multiple degrees of rotational freedom of the alkyl chains that would be lost by internal hydrogen bonding in **H₂4**; 5) the inefficient solvation of internal or congested surfaces of an interpenetrated architecture means that desolvation of binding sites is likely to occur at a lower energetic cost than for conventional structures. All of these factors effectively do the same thing, that is, raise the energy of the rotaxane with respect to the free components. However, the kinetic stabilization of the architecture provided by the stoppers prevents dethreading (the rotaxane is not in equilibrium with the free components). This increase in free energy is actually a form of host preorganization, which serves to enhance binding properties as outlined by Cram over 30 years ago.^[10] The result is that interactions which are not strong enough to stabilize a host–guest complex can become thermodynamically favorable if the components are held together by a mechanical bond (Figure 1).

We reasoned that it should be possible to disrupt the intercomponent hydrogen-bonding interaction in **H₂1** by protonation of the more basic 2,6-dioxymethylenepyridine nitrogen atom (Scheme 1). Although treatment of **H₂1** with one equivalent of trifluoromethanesulfonic acid (TfOH) resulted in protonation of the desired site (Figure 4d), the downfield shift of the H_C amide protons indicated that strong hydrogen bonding was still present. The shielding and broadening of particular thread signals at 298 K (Figure 4d) suggests that instead of residing over the pyridine residue as in **H₂1**, the macrocycle is displaced to the side and shuttles between the two halves of the thread relatively slowly on the



Scheme 1. Binding modes observed for [2]rotaxane $H_2.1$. All of the complexation reactions are fully reversible. A similar range of complexes are exhibited by [2]catenane $H_2.2$ (for an X-ray crystal structure of $Pd2$, see ref. [12]). The hydrogen bonding in $[Pd(H_2.1)Cl_2(MeCN)]$ is observed only in the solid state. Tf = trifluoromethanesulfonyl, DMF = *N,N*-dimethylformamide.

NMR timescale. This was confirmed by the 1H NMR spectrum recorded at 238 K (Figure 4e) in which many of the thread resonances were split into two inequivalent sets (H_b/H_b' , H_c/H_c' , H_d/H_d' , H_e/H_e') that correspond to solvent-exposed and encapsulated (and thus magnetically shielded by the macrocycle) protons, respectively. The rationale for this behavior was provided by the crystal structure of single crystals grown from acetonitrile (Figure 5a). The [2]rotaxane acts as a host for an entire molecule of TfOH; one component (the thread) deprotonates the acid, and both components hydrogen bond to the resulting anion to generate a neutral complex, $H_2.1 \cdot HOTf$. The X-ray crystal structure is consistent with the specific shielding effects seen in the 1H NMR spectra, including the upfield shift of the signal for the pyridinium proton (see Figure 4c) as a consequence of other hydrogen-bond donors binding to the triflate anion, and with the noncovalent binding of the sulfonic acid acting as a transient steric barrier to shuttling of the macrocycle between the two halves of the thread.^[12] In contrast (Scheme 2), a 1:1 mixture of $H_2.3a$ and $3bH^+TfO^-$ in $CDCl_3$ shows neither upfield shift of resonances H_c , H_d , and H_e (compare Figure 4b with the spectrum of the protonated thread in Figure 4c) nor downfield shifts of the protons from the amide groups in $H_2.3a$. Similarly, the absence of shifts in the amide resonances of the protonated covalently linked structure $H_2.4H^+TfO^-$ suggests that it does not internally associate through hydrogen bonding.

The mechanically interlocked assemblies also differ from their noninterlocked counterparts in their ability to adopt a range of overall neutral binding modes with metals. Treatment of $H_2.1$ or $H_2.2$ with $Cu(OAc)_2$ in $MeOH/CH_2Cl_2$ with heating at reflux resulted in double deprotonation of the ligand and the generation of the corresponding 1:1 neutral metal-interlocked ligand complex. Recrystallization of the copper [2]rotaxane complex, $Cu1$, from acetonitrile gave single crystals that were suitable for X-ray crystallographic studies (Figure 5b). The solid-state structure shows a square-based pyramidal coordination motif that involves one of the thread oxygen atoms as well as the four nitrogen atoms of the rotaxane which form the near-planar base of the pyramid (N47 lies approximately 10° above the plane defined by N2–N11–N5–Cu). Treatment of $H_2.3a/3b$ or $H_2.4$ with $Cu(OAc)_2$ under the same conditions gave no indication of formation of a complex nor deprotonation of the amide groups of the macrocycle.

The synthesis of complexes of the mechanically interlocked ligands with nickel required more vigorous conditions ($[Ni(dmf)_6](ClO_4)_2$, NaH, DMF, $60^\circ C$, 1 h) but nonetheless resulted in $Ni1$ and $Ni2$, both isolated as orange crystalline compounds. In this case, a similarly colored complex could also be generated with $H_2.3a/3b$, but unlike $Ni1$ or $Ni2$ the isolated compound rapidly decomposed and we were unable to isolate or characterize it. The X-ray crystal structure of single crystals of $Ni1$ grown from slow cooling of a saturated

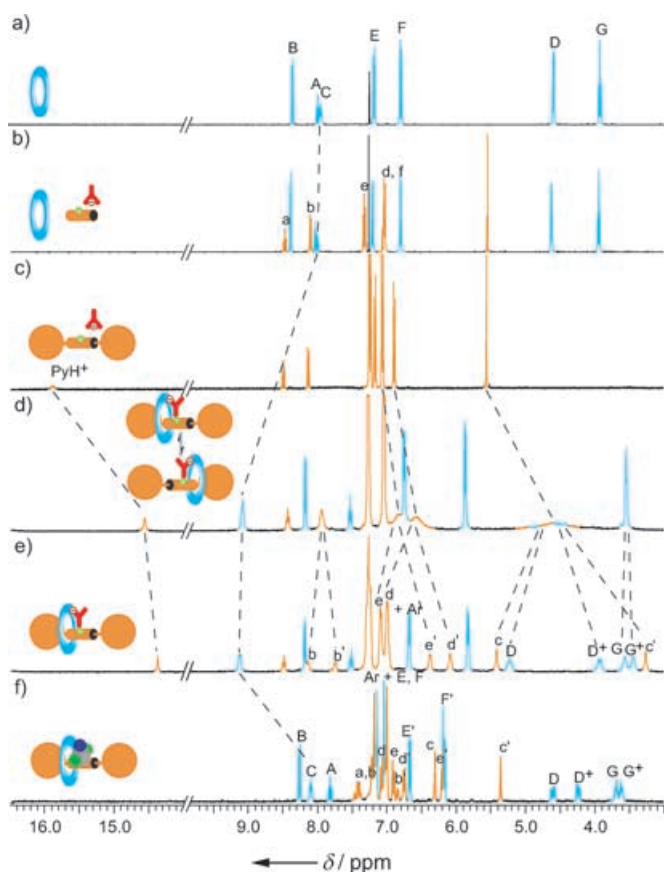


Figure 4. ^1H NMR spectra (CDCl_3 , 400 MHz, 298 K unless otherwise stated): a) macrocycle $\text{H}_2\mathbf{3a}$; b) $\text{H}_2\mathbf{3a}$ and unstopped thread $\mathbf{3b}$ and HOTf; c) thread and HOTf (Py = pyridine); d) [2]rotaxane complex $\text{H}_2\mathbf{1}$ -HOTf showing fast exchange (shuttling) of the macrocycle between equivalent sites on both halves of the thread; e) [2]rotaxane complex $\text{H}_2\mathbf{1}$ -HOTf at 238 K showing slow exchange (reversible noncovalent bonding of the triflate anion provides a transient steric barrier to shuttling); f) $[\text{Pd}(\text{H}_2\mathbf{1})\text{Cl}_2(\text{MeCN})]$ showing slow exchange (coordination of $[\text{PdCl}_2(\text{MeCN})]$ provides a fixed steric barrier to shuttling up to at least 325 K). See Figure 2 for atom labeling scheme.

solution in acetonitrile is shown in Figure 5c and is closely related to the structure obtained for $\text{Cu}\mathbf{1}$. Treatment of any of the rotaxane or catenane metal complexes with KCN in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ regenerated the original interlocked molecule, $\text{H}_2\mathbf{1}$ or $\text{H}_2\mathbf{2}$. The differences in both the ease of formation and the stability of the metal complexes with the catenane and rotaxane relative to the noninterlocked ligands is, again,

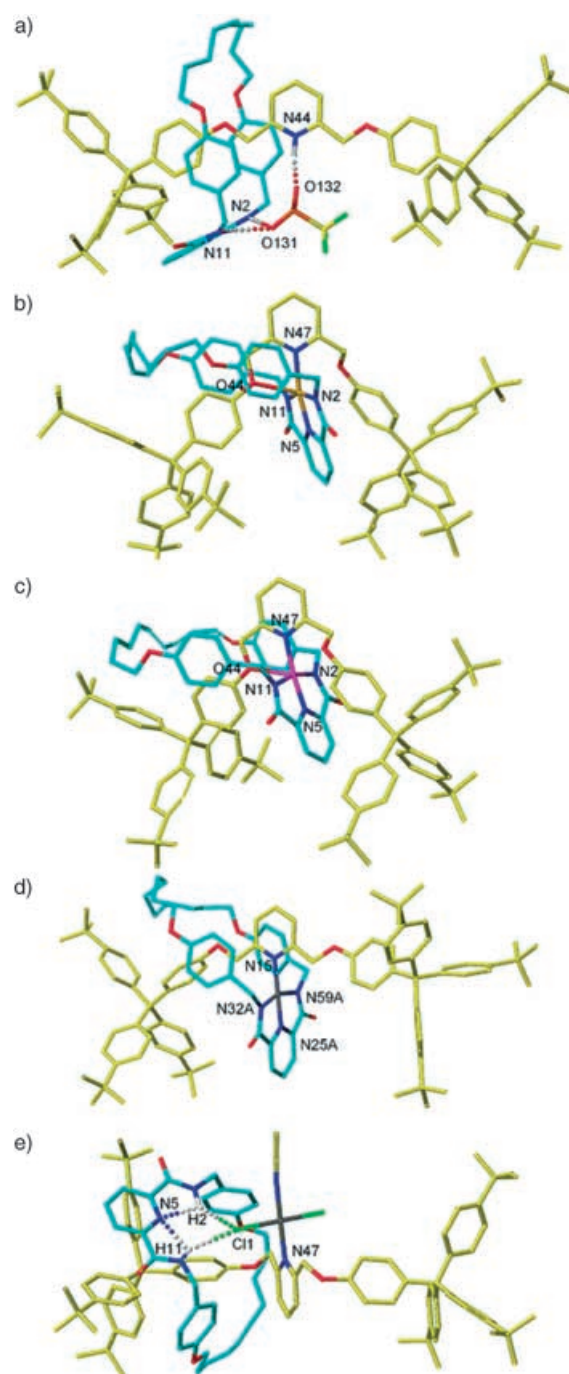
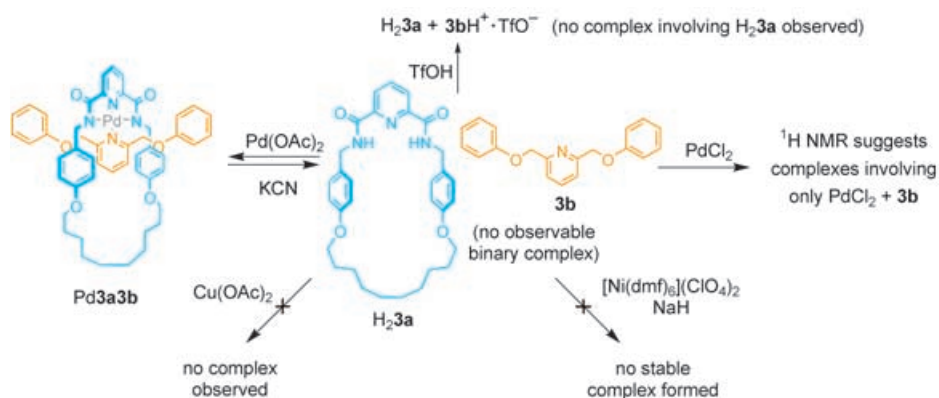


Figure 5. X-ray crystal structures^[7] of various complexes of $\mathbf{1}$: a) neutral [2]rotaxane-triflic acid complex, $\text{H}_2\mathbf{1}$ -HOTf. Note the macrocycle is displaced to one side of the central region of the thread relative to free $\text{H}_2\mathbf{1}$ (Figure 3b); b) square-pyramidal coordination complex $\text{Cu}\mathbf{1}$; c) square-pyramidal coordination complex $\text{Ni}\mathbf{1}$; d) square-planar coordination complex $\text{Pd}\mathbf{1}$; e) square-planar coordination complex $[\text{Pd}(\text{H}_2\mathbf{1})\text{Cl}_2(\text{MeCN})]$. C (macrocycle) turquoise; C (thread) yellow; O red; N dark blue; H white; S orange; F light green; Cl dark green; Cu tan; Ni pink; Pd dark gray. For clarity only amide hydrogen atoms are shown. Selected hydrogen-bond lengths [Å] for $\text{H}_2\mathbf{1}$ -HOTf: N2H–O131 2.14; N11H–O131 2.17; N44H–O132 1.72. Selected bond angles [°] for $\text{H}_2\mathbf{1}$ -HOTf: N2H–O131 159.0; N11H–O131 148.1; N44H–O132 159.7. Selected bond lengths [Å] for $\text{Cu}\mathbf{1}$: N2–Cu 2.00; N11–Cu 1.98; N5–Cu 1.92; N47–Cu 2.02; O44–Cu 2.41. Selected bond angles [°] for $\text{Cu}\mathbf{1}$: N2–Cu–N5 80.3; N5–Cu–N11 80.7; N11–Cu–N47 101.3; N5–Cu–O44 116.6; N5–Cu–N47 169.7. Selected bond lengths [Å] for $\text{Ni}\mathbf{1}$: N2–Ni 1.94; N11–Ni 1.93; N5–Ni 1.81; N47–Ni 1.93; O44–Cu 2.52. Selected bond angles [°] for $\text{Ni}\mathbf{1}$: N2–Ni–N5 82.6; N5–Ni–N11 82.4; N11–Ni–N47 98.5; N5–Ni–O44 113.8; N5–Ni–N47 172.1. Selected bond lengths [Å] for $\text{Pd}\mathbf{1}$: Pd–N15 1.95, Pd–N25 1.86, Pd–N32 2.04, Pd–N59 2.02, N15–N25 3.81. Selected bond angles [°] for $\text{Pd}\mathbf{1}$: N59–Pd–N32 160.0. Selected bond lengths [Å] for $[\text{Pd}(\text{H}_2\mathbf{1})\text{Cl}_2(\text{MeCN})]$: Pd–N47 1.98, Pd–Cl1 2.27, Cl1–H2 2.67, Cl1–H11 2.64, N5–H2 2.36, N5–H11 2.15. Selected bond angles [°] for $[\text{Pd}(\text{H}_2\mathbf{1})\text{Cl}_2(\text{MeCN})]$: N2–H2–Cl1 139.8, N11–H11–N5 114.1, N11–H11–Cl1 125.0.



Scheme 2. Attempted complexation experiments involving $\text{H}_2\text{3a/3b}$. Similar results were obtained with macrocycle $\text{H}_2\text{4}$ (for an X-ray crystal structure of Pd4 , see ref. [12]).

consistent with the intrinsic effect of kinetic stabilization of a mechanically interlocked architecture (Figure 1 c).

Each of the four ligand sets reacts with Pd(OAc)_2 ($\text{H}_2\text{1}$, $\text{H}_2\text{2}$, and $\text{H}_2\text{4}$ directly in $\text{MeCN/CH}_2\text{Cl}_2$; $\text{H}_2\text{3a/3b}$ requires preliminary reaction of Pd(OAc)_2 with $\text{H}_2\text{3a}$ in MeCN followed by treatment of the resulting complex with 3b in CH_2Cl_2) to give the corresponding square-planar coordination complexes (Schemes 1 and 2 and Figure 5 d). However, the rotaxane and catenane also formed a different type of neutral square-planar coordination complex when treated with PdCl_2 , an initial palladium salt that features significantly stronger coordinating ligands (chloride is also less basic than acetate). Slow cooling of saturated solutions of either complex in acetonitrile afforded crystals that were suitable for X-ray crystallography, and the structure of the rotaxane complex, $[\text{Pd}(\text{H}_2\text{1})\text{Cl}_2(\text{MeCN})]$, is shown in Figure 5 e (the solid-state structure of the [2]catenane complex is similar but features intermolecular rather than intramolecular $\text{NH}\cdots\text{Cl}\cdots\text{Pd}$ hydrogen bonding). From the crystal structures it can be seen that although Pd coordinates to the thread as in Pd1 , the original metal chloride ligands remain intact and the macrocycle amides are not deprotonated. In solution the coordination of the $[\text{PdCl}_2(\text{MeCN})]$ unit to the pyridine ring of the thread acts as a steric barrier to shuttling (Figure 4 f). This is similar to the effect seen with $\text{H}_2\text{1}\cdot\text{TfOH}$, but unlike the complex held together by hydrogen bonds the coordination to the metal is not kinetically labile and persists as a barrier to shuttling up to at least 325 K (close to the boiling point of the solvent CDCl_3).^[11]

The solid-state structure of $[\text{Pd}(\text{H}_2\text{1})\text{Cl}_2(\text{MeCN})]$ features hydrogen bonding between the amide groups of the macrocycle and the chloride ligands of the metal (Figure 5 e). However, the ^1H NMR spectrum shows that this interaction is not present to any significant extent in CDCl_3 (the chemical shift of H_C is virtually unchanged compared to $\text{H}_2\text{3a}$, Figure 4 f). Wisner and co-workers recently used a similar interaction to direct an elegant synthesis of a pseudorotaxane.^[13] During the course of that work, a macrocycle binding constant that largely results from two sets of isophthalamide

groups hydrogen bonding to the chloride ligands of a Pd^{II} complex was determined to be $5 \times 10^3 \text{ M}^{-1}$ in CDCl_3 .^[13] In contrast, Crabtree and co-workers determined the association constant for a single isophthalamide group with Cl^- to be $6 \times 10^4 \text{ M}^{-1}$ in CD_2Cl_2 .^[14] Accordingly, a $\text{C(O)NH}\cdots\text{Cl}\cdots\text{Pd}$ interaction must be somewhat less than half the strength of a $\text{C(O)NH}\cdots\text{Cl}^-$ hydrogen bond. This is consistent with the observation that the interaction is too weak to significantly bind the macrocycle in $[\text{Pd}(\text{H}_2\text{1})\text{Cl}_2(\text{MeCN})]$ in CDCl_3 , despite the high effective molarity introduced by the mechanical bond, and is in marked contrast to the effective bifurcated pyridine–pyridine hydrogen bonding in $\text{H}_2\text{1}$. This suggests that the intercomponent binding mode in $\text{H}_2\text{1}$ is not particularly weak and its scarcity as an observed interaction may arise because the geometry of the interlocked architecture precludes otherwise preferred noncovalent bonding geometries.

In conclusion, the kinetically enforced association of molecular fragments within an interlocked architecture facilitates the formation of diverse, and sometimes rare and unusual, binding motifs both in solution and the solid state. These interactions can produce interesting effects in their own right; the cooperative hydrogen bonding of an organic guest by both components of a [2]rotaxane can present an effective barrier to shuttling at low temperatures, whereas a stronger metal–ligand coordination mode can be used to restrict the same motion even at higher temperatures. The fact that many of the observed modes of binding are weaker or not seen at all when the components are not mechanically interlocked makes this consequence of the mechanical bond particularly noteworthy.^[15]

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- [15] *Note added in proof*: A paper recently appeared (Y. Furusho, T. Matsuyama, T. Takata, T. Moriuchi, T. Hirao, *Tetrahedron Lett.* **2004**, *45*, 9593–9597) that reproduces some of the previous work^[3] on the square-planar template rotaxane system. Although the authors do not comment on it, the ¹H NMR chemical shifts show that the bifurcated pyridine–pyridine hydrogen-bonding motif also exists in their demetalated rotaxane.