

Controlling the ON/OFF threading of a terpyridine containing [2]pseudorotaxane ligand *via* changes in coordination geometry†

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A 1,2-bis(pyridinium)ethane type axle containing a terpyridine chelate group, when combined with 24-membered crown ethers, forms [2]pseudorotaxanes, the stability of which can be controlled by coordination of metal ions with different geometries.

Control of the ON/OFF threading and unthreading of [2]pseudorotaxanes can be thought of as a crude type of molecular switch.¹ The ON and OFF states are based on two different positions of the molecular recognition equilibrium that involves the interpenetration between axle and wheel. A number of methods have been devised to control this equilibrium with the most common being acid–base chemistry² and electrochemistry.³

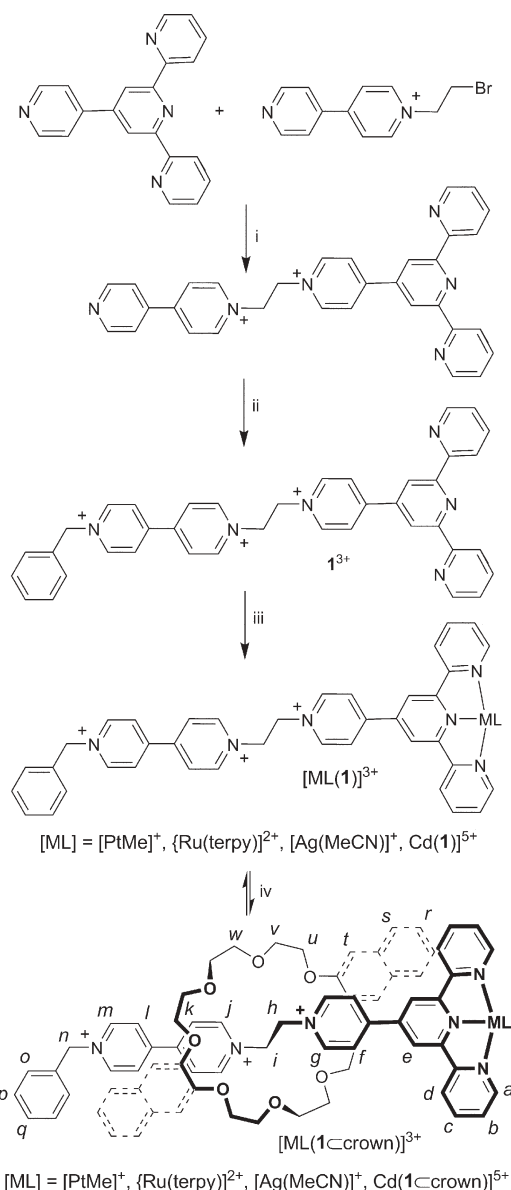
We are interested in the use of [2]pseudorotaxanes⁴ and [2]rotaxanes⁵ as ligands and have prepared a number of coordination complexes⁶ and metal–organic rotaxane frameworks⁷ (MORFs) using this concept. One of our goals has been to create rotaxanes that could be easily used as ligands without the need for special preparative conditions and to this end we prepared rotaxanes containing a classical tridentate terpyridine (terpy) group.⁶ These rotaxane ligands were found to be quite robust and their coordination chemistry with Fe(II)^{6b} and Ru(II)^{6c} has been reported. During these studies, we noted that the steric requirements of the terpy ligand unit changed dramatically upon complex formation and the extent to which this affected the interaction between axle and wheel varied widely.

Herein, we describe a fundamental study on the association between the terpy ligand axle 1^{3+} and its transition metal complexes with various 24-membered crown ethers, 24-crown-8 (**24C8**), dibenzo-24-crown-8 (**DB24C8**) and dinaphtho-24-crown-8 (**DN24C8**). In particular, we demonstrate that the equilibrium position between axle/wheel and [2]pseudorotaxane can be manipulated by the coordination geometry of the terpy group attached to the axle.⁸

The axle 1^{3+} was prepared as outlined in Scheme 1 and the transition metal complexes prepared by reaction with appropriate starting materials. We initially chose to compare [2]pseudorotaxane formation for the ligand 1^{3+} with the square planar complex [PtMe(I)]⁴⁺ and the octahedral complex [Ru(terpy)(1)]⁵⁺. Pt(II) and Ru(II) were selected as they both provide robust, inert complexes for which metal ligand exchange would be essentially non-existent in a non-competitive solvent such as MeNO₂.

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Scheme 1 (i) MeCN reflux, 7 days, anion exchange with [NaBF₄]; (ii) 5 equiv. benzyl bromide, MeCN reflux, 72 h, anion exchange with [NaBF₄]; (iii) one equiv. each of [PtCIME(Me₂S)₂] and [Ag][BF₄], 50 °C in MeOH, 24 h; [Ag][BF₄] in MeCN, rt, 1 h; [RuCl₃(terpy)], reflux in EtOH–H₂O, 12 h; 0.5 equiv. [Cd(H₂O)₆][BF₄]₂, MeOH–MeCN, rt, 1 h; (iv) 1 equiv. of a 24-membered crown ether, **24C8**, **DB24C8** or **DN24C8** in MeCN-*d*₃ at 2.0 × 10⁻³ M. Labels refer to NMR spectral assignments.

Table 1 A comparison of K_a (M^{-1}) ($\Delta G^\circ/kJ\ mol^{-1}$) values for [2]pseudorotaxanes in CD_3CN solution (2.0×10^{-3} M) at 298 K^a

Axle	Crown ether wheel		
	24C8	DB24C8	DN24C8
I^{3+}	146 (-12.8)	569 (-16.9)	1242 (-18.8)
[PtMe(1)] ⁴⁺	168 (-13.3)	431 (-16.1)	2054 (-20.4)
[Ru(terpy)(1)] ⁵⁺	80 (-11.4)	245 (-14.2)	392 (-16.2)
[Ag(MeCN)(1)] ⁴⁺	189 (-13.2)	502 (-16.4)	1444 (-19.1)
[Cd(1) ₂] ⁸⁺	111 (-12.5)	621 (-17.2)	497 (-16.4)

^a All spectra were observed to be undergoing exchange that was slow on the NMR time scale. Errors were estimated to be <10% for values measured by the single point method using integrations from these NMR spectra.

Table 1 summarizes the association constants for [2]pseudorotaxane formation between the various axles and the three crown ethers. The previously observed trend for this type of benzylated axle was an increase in K_a with increased π -stacking; **24C8** < **DB24C8** < **DN24C8**.^{4b} Data from Table 1 show that when [2]pseudorotaxanes are formed with **24C8** or **DB24C8** there is no deviation from this trend and there is no significant difference in the association between free ligand, square planar complex or octahedral complex. However, when **DN24C8** is used as the wheel there are quite dramatic differences which do not match the typical trend and appear to correlate with the coordination geometry of the complex. For example, the association constant for [1**CDN24C8**]³⁺ is $\sim 1200\ M^{-1}$ but this is reduced to $\sim 400\ M^{-1}$ for the octahedral complex [Ru(terpy)(1**CDN24C8**)]⁵⁺ and increased substantially to $\sim 2000\ M^{-1}$ for the square planar complex [PtMe(1**CDN24C8**)]⁴⁺.

The rationale for this is fairly straightforward. The naphtho group of **DN24C8** extends far enough into the coordination environment of the ligand to be affected by that local geometry; this does not occur for **24C8** and **DB24C8**. For the octahedral Ru(II) complex, this results in steric interactions between the crown ether naphtho ring and the ancillary terpy ligand which lowers the K_a . For the square planar compound, the presence of the Pt(II) fragment provides for increased π -stacking between the extended electron-poor aromatic surface which enhances the K_a . These two scenarios are illustrated in Fig. 1.

With the effect of coordination geometry established using these inert Ru(II) and Pt(II) complexes, it was of interest to mimic this effect with more labile metals. This would potentially allow for the conversion between the ON and OFF states of the [2]pseudorotaxanes by exchanging one type of metal coordination environment (octahedral) for another (square planar) in much the same way that other systems have been controlled by pH.³ To this end, we prepared the square planar complex [Ag(MeCN)(1)]⁴⁺ as an analogue for [PtMe(1)]⁴⁺ and the bis-ligand octahedral complex [Cd(1)₂]⁸⁺ as an analogue for [Ru(terpy)(1)]⁵⁺. The new complexes were combined with equimolar amounts (2.0×10^{-3} M) of the three crown ethers and ¹H NMR spectroscopy was used to determine the association constants for each resulting [2]pseudorotaxane. All of the equilibria were slow on the NMR time scale at all measured temperatures. Fig. 2 illustrates the effect of the sequential addition of [Ag(MeCN)]⁺ and **DN24C8** to axle **1**³⁺ as monitored by ¹H NMR spectroscopy.

A summary bar graph displaying association constants as a function of complexed metal fragment is shown in Fig. 3. It is clear

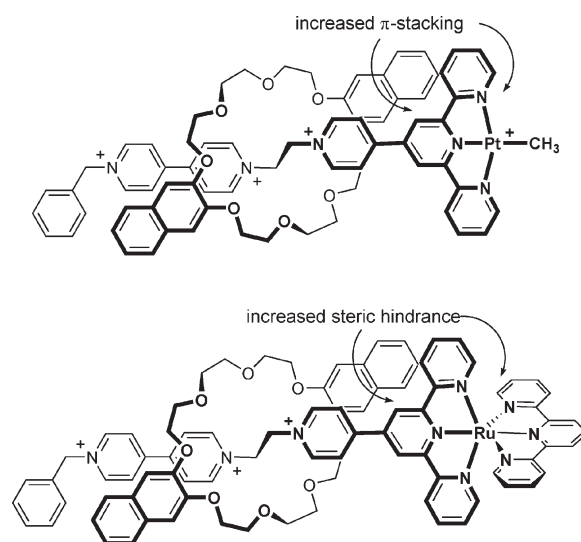


Fig. 1 Association between axle and wheel is dependent on the coordination geometry. Top: a square planar Pt-CH₃ complex provides a large electron-poor surface for π -stacking with the naphtho ring. Bottom: an octahedral Ru-terpy complex causes steric interactions between the ancillary terpy ligand and the naphtho unit.

that when [2]pseudorotaxanes are formed using **DN24C8**, the square planar complexes of Ag(I) and Pt(II) show an increased association, whereas the presence of an octahedral centre using

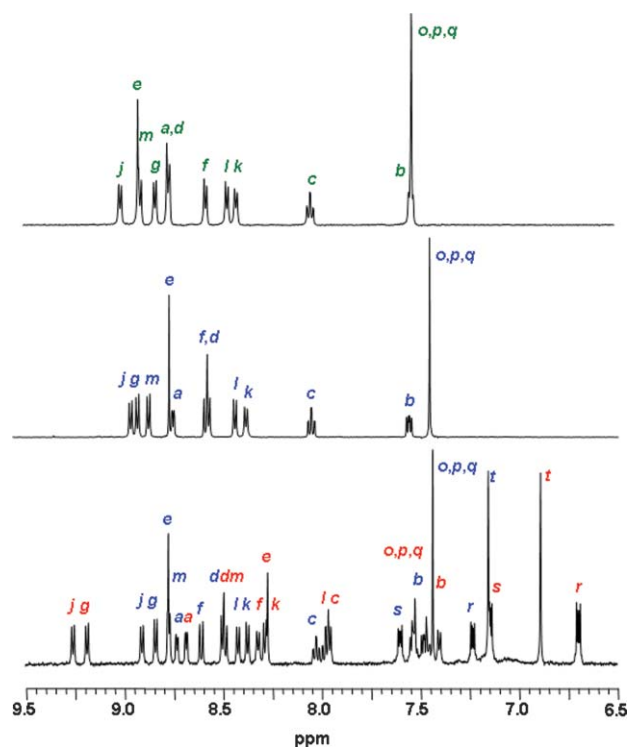


Fig. 2 ¹H NMR spectra—downfield portion (500 MHz, 300 K, CD_3CN , 2.0×10^{-3} M). Top: the free ligand **1**³⁺ (green labels). Middle: the complex [Ag(MeCN)(1)]⁴⁺ (blue labels). Bottom: an equilibrium mixture of the [2]pseudorotaxane [Ag(MeCN)(1**CDN24C8**)]⁴⁺ (red labels), [Ag(MeCN)(1)]⁴⁺ (blue labels) and **DN24C8** (blue labels). See Scheme 1 for proton assignments.

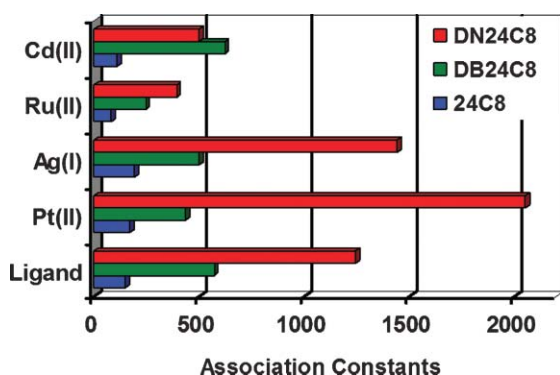
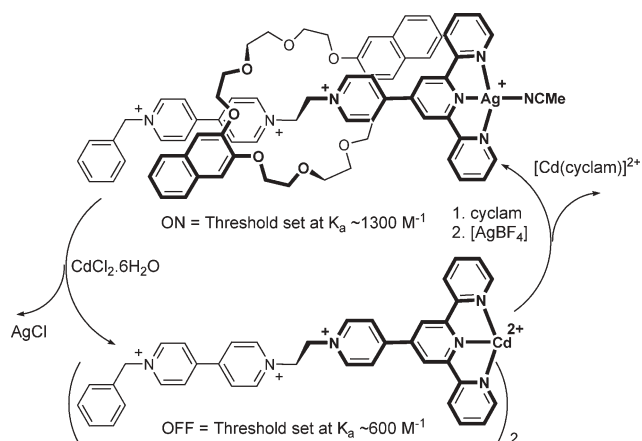


Fig. 3 A plot of association constant (M^{-1}) for the formation of [2]pseudorotaxane as a function of crown ether and coordinated metal (2.0×10^{-3} M in CD_3CN at 298 K).



Scheme 2 Exchanging between Ag(I) and Cd(II) ions results in an ON/OFF chemical cycle controlled by the coordination environment (square planar *versus* octahedral) at the chelating terpy site.

Ru(II) and Cd(II) resulted in a decreased association between the wheel and axle.

Finally, as designed, the Ag(I) and Cd(II) complexes were employed in a cycle of ON/OFF switching by exchanging metal ions and thus varying coordination environment at the terpy site. Arbitrary thresholds of $K_a > 1300 M^{-1}$ and $K_a < 600 M^{-1}$ were set to represent the requirements for the threaded state (ON) and unthreaded state (OFF) respectively. Initially, an equilibrium mixture containing the [2]pseudorotaxane ligand $[1CDN24C8]^{3+}$ was reacted with $[Ag][BF_4]$ in CD_3CN in an NMR tube to produce $[Ag(CD_3CN)(1CDN24C8)]^{4+}$; designated the ON state. This complex was then treated with half an equivalent of $CdCl_2 \cdot 6H_2O$ which resulted in the precipitation of $AgCl(s)$ and formation of the [2]pseudorotaxane $[Cd(1CDN24C8)_2]^{8+}$; the OFF state. Subsequent treatment with one equivalent of the well known macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam)⁹ resulted in quantitative removal of the Cd^{2+} ion¹⁰ and regeneration of the free ligand $[1CDN24C8]^{3+}$ which could then be recycled to the ON state by adding $[Ag][BF_4]$; see Scheme 2. This effectively creates a cycle that can be fully controlled by the coordination environment at the chelated transition metal ion; in this case Ag(I) and Cd(II).

This cycle of metal addition and elimination was repeated three times without significant decomposition of the ligand components.

In summary, when the axle of a [2]pseudorotaxane is constructed such that it contains a chelating end group the resulting ligand can be easily coordinated to a transition metal ion. In our particular design described herein, the metal chelating site and the recognition site for the wheel overlap. As such, the threading of the wheel component may be influenced by the coordination of a metal ion. We have shown here that the geometry of the metal coordination site can be used to control the association constant for [2]pseudorotaxane formation and, when the metal ions are exchangeable, control the ON/OFF threading of a sufficiently large crown ether (DN24C8). This type of chemical control using coordination chemistry should also be applicable to suitably designed molecular shuttles and other molecular switches based on interlocked molecules. We are currently preparing such materials.

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