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Rotationally Active Ligands: Dialing-Up the Co-conformations of a [2]Rotaxane for Metal Ion Binding

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Abstract: *A novel [2]rotaxane was constructed that has a bidentate N,N′-chelate as part of a rigid, H-shaped axle and a 24-membered crown ether macrocycle containing six ether O-atoms and an olefinic group as the wheel. This unique topology produces a ligand with the ability to dial-up different donor sets for complexation to metal ions by simply rotating the wheel about the axle. The solution and solid-state structures of the free ligand and complexes with Li^+ and Cu^+ show how the ligand adopts different rotational co-conformations for each. The Li^+ ion uses the N,N′-chelate and O-donors while the Cu^+ center is coordinated to both O-donors and the olefinic group. This concept of rotationally active ligands should be possible with a wide variety of donor sets and could find broad application in areas of coordination chemistry, such as catalysis and metal sequestration.*

One of the pioneering methods for the preparation of mechanically interlocked and topologically non-trivial molecules, such as catenanes, rotaxanes, and molecular knots, involved the use of transition metal ion templates.[1] Most notably the utilization by Sauvage of tetrahedral Cu^I complexes with orthogonally positioned 1,10-phenanthroline ligands.[2] Although these types of templates have been subsequently exploited to make, for example, higher-order knots,[3] redox and light switchable mechanically interlocked molecules (MIMs),[4] there has been very little research into exploiting the interlocked topology of MIMS for ligand design in applications such as selective metal ion sequestration[5] or catalysis.[6] In particular, we were intrigued by the possibility of organizing disparate donor sets into the three-dimensional cavity created between a linear axle and a macrocyclic wheel of a [2]rotaxane. The interlocked nature of the system provides the possibility of rotating the macrocyclic wheel relative to the axle and preferentially dialing-up donor sets utilizing different co-conformations of the MIM. This concept of a rotationally active ligand is outlined in Figure 1.

We chose an initial design based on our recent success in preparing rigid [2]rotaxane linkers for incorporation into metal–organic frameworks (MOFs).[7] Terphenylene struts, such as those shown in Figure 1, have been successfully combined with benzimidazolium recognition sites and 24-membered crown ethers to create effective [2]rotaxane molecular shuttles.[8] By removing the spacer group used to separate the recognition sites, we can generate an axle in which two benzimidazole groups are directly bonded to each other resulting in a single recognition site that is a bidentate, *N,N′*-chelate. Scheme 1 outlines how this new chelating axle was prepared and a macrocyclic crown ether wheel clipped around it employing Grubbs' ring-closing metathesis (RCM) to yield a [2]rotaxane ligand (**L**).[9] Herein, we demonstrate that this type of ligand can coordinate to different metals by utilizing the axle chelate and rotating the macrocycle to access the most suitable donor set. Importantly, given the variety of known macrocyclic ligands and the excellent templating ability of this orthogonal approach, this concept of rotationally active ligands might be useful for an assortment of chemical applications.

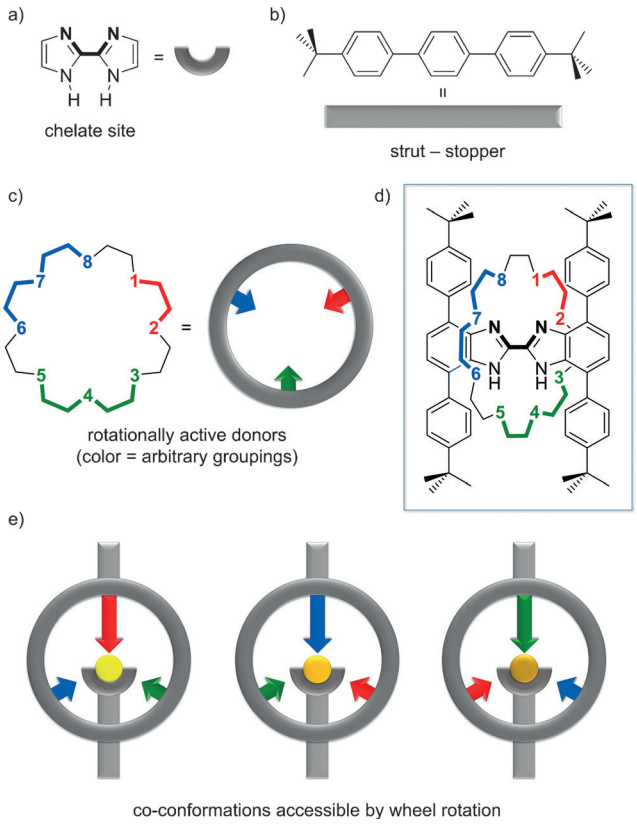

Figure 1. a) An axle with a chelating site, b) struts as stoppers, c) a macrocycle with donor atoms, d) a rotationally active ligand (three arbitrary color sets are shown for illustrative purposes), e) three co-conformations for coordination to a metal ion via rotation of the macrocycle wheel. The long arrow represents direct coordination while shorter arrows represent weaker second-sphere interactions.

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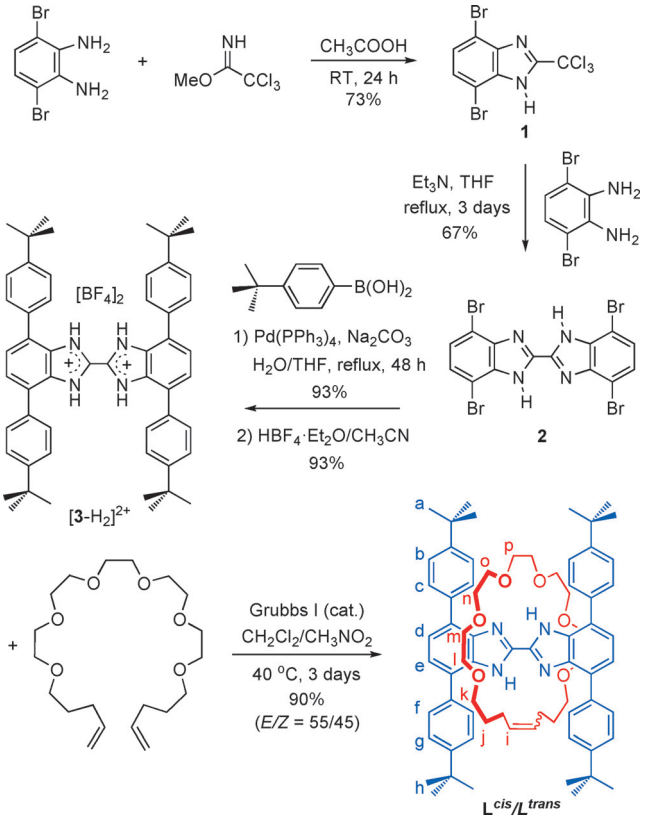

Scheme 1. Preparation of a mixture of [2]rotaxane ligands $\mathbf{L}^{cis}$ and $\mathbf{L}^{trans}$ via Grubbs' RCM.

The isolated mixture of $\mathbf{L}^{cis}$ and $\mathbf{L}^{trans}$ was initially screened for binding with alkali metal cations using UV/Vis and NMR titrations. Of the alkali metals, only the smallest was bound significantly in the predictably tight pocket between axle and wheel, Li^+ ($r = 0.90$ Å, $\log K = 5.95\,M^{-1}$), Na^+ ($r = 1.16$ Å, $\log K = 2.63\,M^{-1}$), K^+ ($r = 1.52$ Å, $\log K < 0.1\,M^{-1}$); larger ions resulted in only small changes in chemical shift and broad resonances that were interpreted as weak external interactions with crown ether oxygen atoms only. Given this size selectivity, a similar sized transition metal cation was screened; Cu^+ ($r = 0.91$ Å, $\log K = 3.29\,M^{-1}$) also appeared to be suitable for coordination to the $\mathbf{L}^{cis}/\mathbf{L}^{trans}$ ligand mixture.

A surprising observation was made from the ^{1}H NMR spectrum of the $\mathbf{L}^{cis}/\mathbf{L}^{trans}$ mixture upon the addition of an excess of Cu^I ions. It was apparent that the olefinic double bond of only one of the isomers was participating in coordination to the metal center, while the other isomer was becoming protonated. Cu^I olefin complexes are well-known,[10] but this significant difference in behavior of two closely related species was puzzling. It was also reasoned that this difference in coordination chemistry might be used to separate the two isomers. To this end, preparative TLC plates (see the Supporting Information) were pre-treated with a solution of Cu^I ions in CH_3CN and the mixture eluted with a 9:1 (v:v) $CHCl_3$:CH_3CN solution. One isomer appeared to have no interaction with the Cu^I ions and eluted close to the solvent front while the other isomer eluted more slowly (R_f values: $\mathbf{L}^{cis}$ 0.78, $\mathbf{L}^{trans}$ 0.45). This method was then applied to a larger scale, separation by column chromatography on Cu^I-adsorbed silica (see the Supporting Information). Although the adsorption of Cu^I and Ag^I salts on silica, zeolites, resins, and other solid supports has been exploited for the industrial separation of olefin/paraffin mixtures,[11] and $AgNO_3$-impregnated silica is a powerful tool for the separation of mixtures of unsaturated compounds,[12] there are no reports describing the preparation and use of Cu^I-adsorbed silica for the separation of complex mixtures of olefins by column chromatography. The novelty of this procedure resides in the ease of preparation of the stationary phase and in the high separation efficiency of structurally similar isomers.[13]

Once separated, $\mathbf{L}^{cis}$ and $\mathbf{L}^{trans}$ were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and ESI mass spectrometry. Unambiguous identification was made by single-crystal X-ray diffraction. Figure 2 compares the X-ray structures of isomers

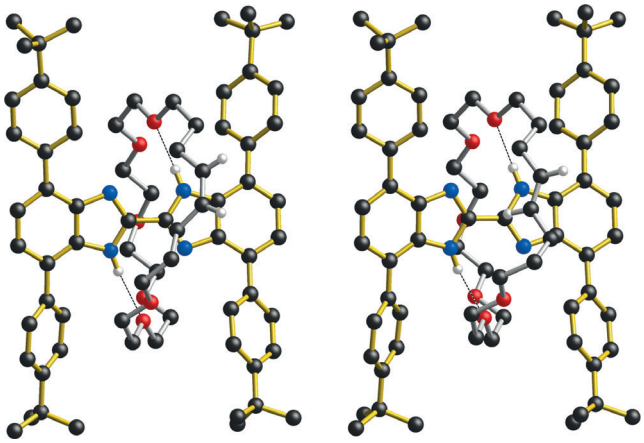

Figure 2. Single-crystal X-ray structures of: left, $\mathbf{L}^{cis}$ and right $\mathbf{L}^{trans}$. O red, N blue, C black; gold bonds = axle, silver bonds = wheel. Only H-atoms involved in H-bonding or part of the olefinic moiety of the macrocycle are shown for clarity.[14]

$\mathbf{L}^{cis}$ and $\mathbf{L}^{trans}$. Both axles are centrosymmetric with the two benzimidazole NH groups involved in H-bonding to the first and fifth ether O-atoms of the 24-membered macrocycle linkage ($\mathbf{L}^{cis}$ NH···O; 2.93 Å (160°) and NH···O; 3.00 Å (160°); $\mathbf{L}^{trans}$ NH···O; 2.93 Å (160°) and NH···O; 2.98 Å (157°).

Figure 3 shows a comparison of the ^{1}H NMR spectra of $\mathbf{L}^{cis}$ and $\mathbf{L}^{trans}$ after addition of an excess of Cu^I (BF_4^- salt). It was determined that $\mathbf{L}^{trans}$ forms a stable complex, $[Cu(\mathbf{L}^{trans})]^+$, while $\mathbf{L}^{cis}$ becomes protonated due to small amounts of water, which in combination with Lewis acidic Cu^I ions and a basic bis-benzimidazole rotaxane, promotes proton transfer. The ^{1}H NMR spectrum of $[Cu(\mathbf{L}^{trans})]^+$ shows that the olefinic H-atoms of $\mathbf{L}^{trans}$ are shifted upfield ($\Delta\delta = -0.93$ ppm), indicating a significant interaction of the double bond with the Cu^I center.

At this juncture, it was of interest to determine exactly how $\mathbf{L}^{trans}$ binds to the most strongly interacting metal cations, Li^+ and Cu^+. Firstly, both $[Li(\mathbf{L}^{trans})]^+$ and $[Cu(\mathbf{L}^{trans})]^+$ were fully characterized in $CDCl_3$ solution by ^{1}H-^{1}H 2D ROESY and ^{1}H-^{1}H 2D COSY NMR experiments. Figure 4 shows the relative positions of the axle and wheel components as

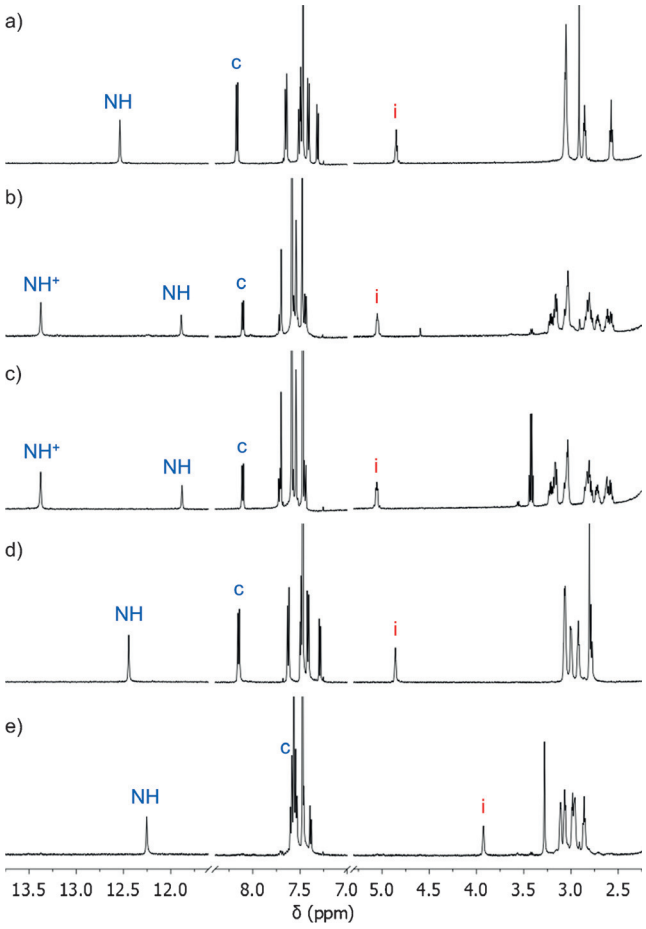

Figure 3. ^{1}H NMR spectra (500 MHz, 298 K, 1:1 CD_3CN:$CDCl_3$) of: a) $\mathbf{L}^{cis}$; b) $\mathbf{L}^{cis}$ after the addition of 30 equiv of $[Cu(CH_3CN)_4][BF_4]$; c) $[H\text{-}\mathbf{L}^{cis}]^+$; d) $\mathbf{L}^{trans}$; e) $\mathbf{L}^{trans}$ after the addition of 30 equiv of $[Cu(CH_3CN)_4][BF_4]$. Only imidazole (NH), olefinic (i) and aromatic (c) protons are labeled; for full assignments, see the Supporting Information.

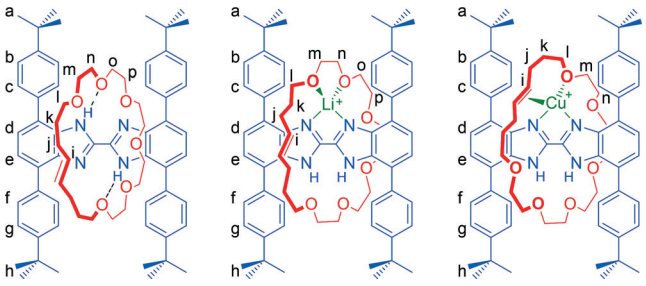

Figure 4. The different co-conformations of the [2]rotaxane ligand $\mathbf{L}^{trans}$ in solution as determined by 2D NMR experiments in $CDCl_3$ for the species: left, neutral $\mathbf{L}^{trans}$; middle, $[Li(\mathbf{L}^{trans})]^+$; right, $[Cu(\mathbf{L}^{trans})]^+$ (see the Supporting Information for details).

determined by the ROE cross-peak analysis of the 2D NMR experiments for the free ligand $\mathbf{L}^{trans}$ and the two complexes $[Li(\mathbf{L}^{trans})]^+$ and $[Cu(\mathbf{L}^{trans})]^+$ (see the Supporting Information).

Secondly, single-crystal X-ray structures were determined for both $[Li(\mathbf{L}^{trans})][BF_4]$ and $[Cu(\mathbf{L}^{trans})][OTf]$. Figures 5 and 6 show the structures of the $[Li(\mathbf{L}^{trans})]^+$ and $[Cu(\mathbf{L}^{trans})]^+$ cations, respectively. The encapsulated metal ions are

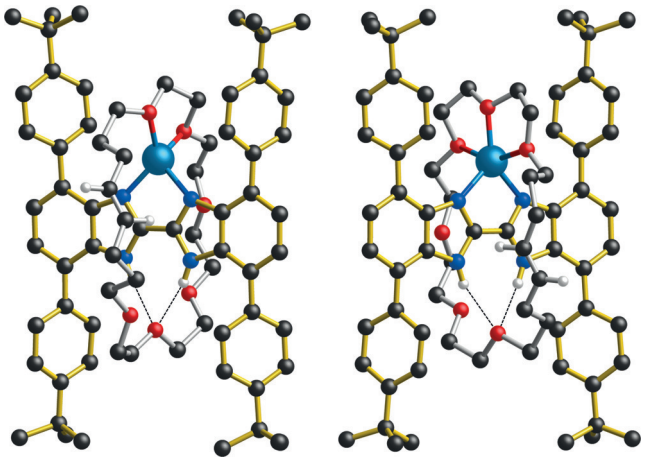

Figure 5. Single-crystal X-ray structure of $[Li(\mathbf{L}^{trans})]^+$: left, N_2O_2 tetrahedral geometry and right, N_2O_3 trigonal bipyramidal geometry. O red, N blue, C black, Li green; gold bonds = axle, silver bonds = wheel. Only H-atoms involved in H-bonding or the olefin are shown and anions are omitted for clarity.[14]

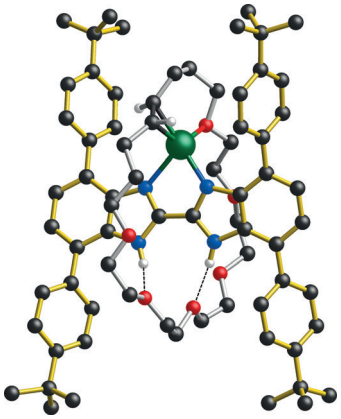

Figure 6. Single-crystal X-ray structure of $[Cu(\mathbf{L}^{trans})]^+$ O red, N blue, C black, Cu teal; gold bonds = axle, silver bonds = wheel. Only H-atoms involved in H-bonding or the olefin are shown and anions are omitted for clarity.[14]

bonded to both the bidentate chelate of the axle and several donor atoms from the wheel. However, the ligand co-conformations used to bind Cu^+ and Li^+ are quite different.

The $[Li(\mathbf{L}^{trans})]^+$ cation displays two distinct co-conformations within the single lattice. In one of the co-conformations, the Li^+ cation adopts a distorted tetrahedral geometry chelating to two O-donor atoms of the macrocycle (Li–O 1.97(2) and 1.92(2) Å) and the two N-atoms from the axle chelate (Li–N 2.03(2) and 2.08(2) Å). In the other co-conformation, the Li^+ center is in distorted trigonal bipyramidal environment coordinating to three O-donor atoms of the macrocycle (Li–O 2.27(2), 2.07(2) and 1.99(2) Å) and the two N-atoms of the axle (Li–N 2.08(2) and 2.09(2) Å).

In stark contrast, for $[Cu(\mathbf{L}^{trans})]^+$ the Cu^+ cation adopts a distorted tetrahedral geometry chelating to the axle (Cu–N 2.013(3) and 2.391(3) Å) but utilizing the olefin moiety of the macrocycle (Cu–C 2.079(4) and 2.050(4) Å), as was originally

inferred by their downfield shift in the ^{1}H NMR spectrum, along with a single O-atom (Cu–O 2.068(3) Å).

Thus, solution and solid state results demonstrate how the interlocked structure of a [2]rotaxane can be utilized to create rotationally active ligands with orthogonal donor sets attached to highly dynamic but independent components. The two major degrees of freedom for $\mathbf{L}^{trans}$ are the facile rotation about the single bond between the two benzimidazole groups and the large amplitude rotation of the 24-membered macrocycle about the rigid H-shaped axle. In the free ligand (Figure 7a), two NH···O hydrogen bonds orient the macrocyclic wheel to optimize these non-covalent interactions. In the complexes (Figure 7b–d), the coordination requirements of the metal ion influences the choice of donors from the macrocycle and residual hydrogen bonds provide complementary second-sphere interactions.

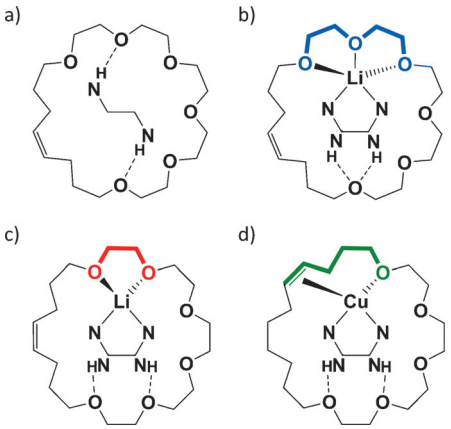

Figure 7. The rotational co-conformations "dialed-up" for the [2]rotaxane ligand: a) neutral ligand $\mathbf{L}^{trans}$, b) and c) Li^+ complexes, d) Cu^+ complex.

This unique combination of a mechanically interlocked structure and flexibility imparts a single ligand with the ability to dial-up the appropriate donor atoms required to form stable complexes of metals cations with very different electronic requirements, in this case Li^+ and Cu^+. A variety of conceptually similar, rotationally active ligands should be possible and may find application in catalysis and metal sequestration.

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[13] Along with *cis* and *trans* isomers of the double bond, there are possible *cisoid* and *transoid* conformations of the *N*,*N*′-imidazole chelate. The latter are easily interconverted by rotation about the single bond between the imidazole groups. Only the *cisoid*, *N*,*N*′-imidazole chelate is used to bind to a metal cation.

[14] CCDC 1496411 – 1496414 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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