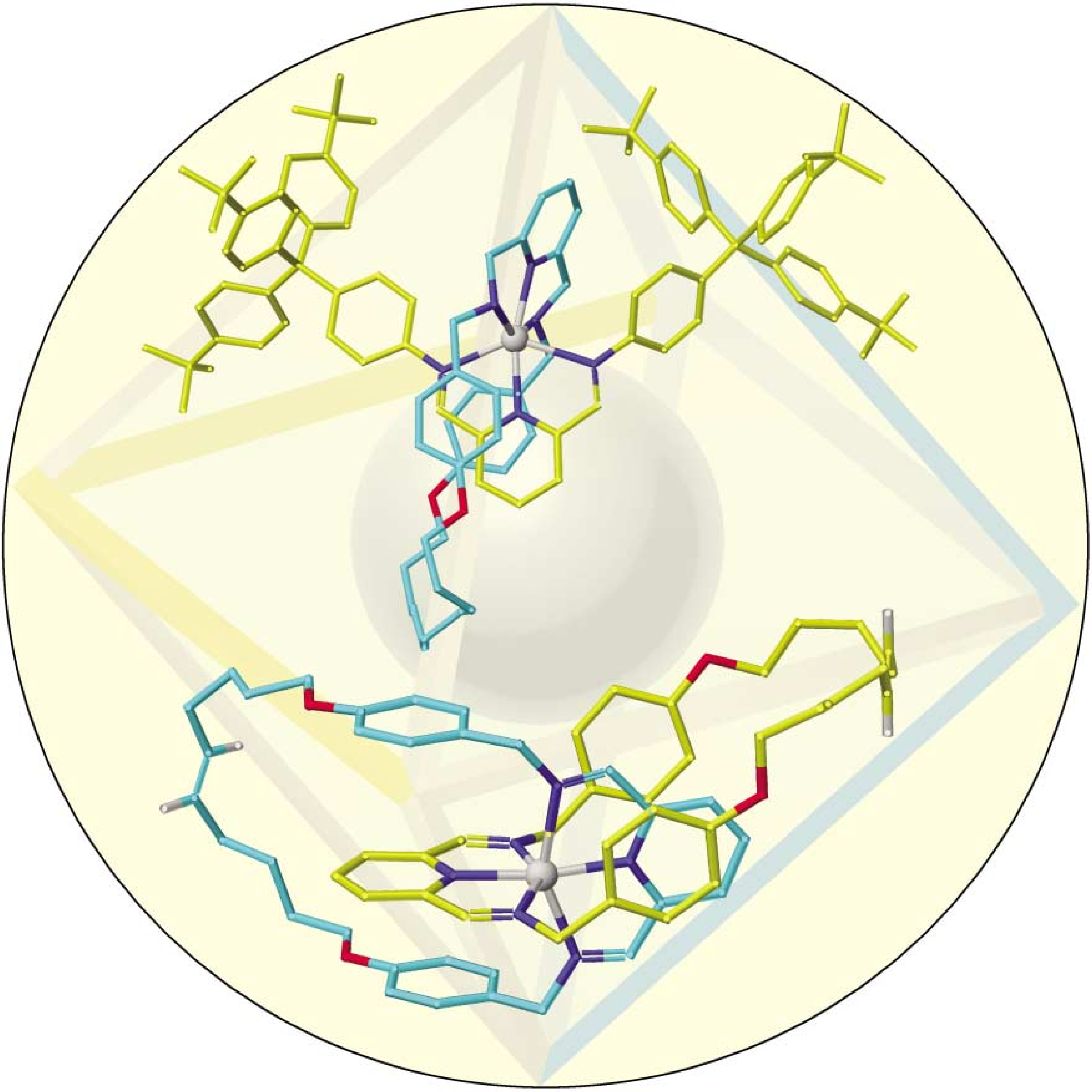
Zuschriften



In ihrer Zuschrift auf den folgenden Seiten beschreiben D. A. Leigh et al. ein allgemeines Ligandensystem für Rotaxankomplexe von Übergangsmetall-Ionen, die die für Rotaxane seltene oktaedrische Koordination bevorzugen. Einfaches Mischen der Komponenten bei Raumtemperatur reicht aus, um eine Vielzahl oktaedrisch koordinierter [2]Metallorotaxane in hohen Ausbeuten zu erhalten.

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Rotaxanes

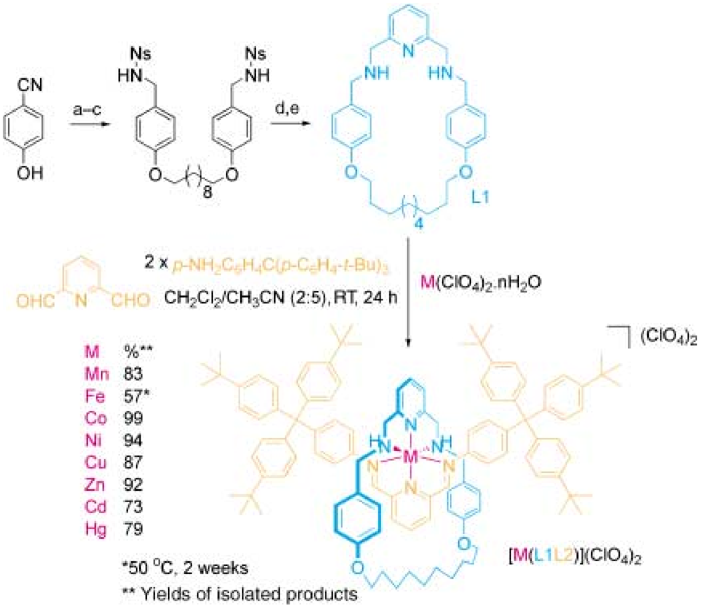
A Simple General Ligand System for Assembling Octahedral Metal–Rotaxane Complexes[**]

Louise Hogg, David A. Leigh,[*] Paul J. Lusby, Alessandra Morelli, Simon Parsons, and Jenny K. Y. Wong

Coordination complexes in which rotaxanes act as ligands for transition-metal atoms are amongst the most celebrated examples of mechanically interlocked molecular level architectures.[1] This is not only because coordination chemistry makes possible a rich diversity of structures, but also because the metal atom can be locked in unusual environments for subsequent electrochemical,[2] photochemical[3] and catalysis[4] studies. Efficient synthetic methods have been developed for rotaxanes based on tetrahedral and trigonal-bipyrimidal metal complexes by using the metal-bis-phenanthroline synthon pioneered in Strasbourg.[1a,b,5] Herein we describe a general ligand system for rotaxane complexes of ions that prefer octahedral coordination—the commonest ligand geometry amongst transition metals, but up to now a rare[6] coordination mode for rotaxanes. Simple mixing of the components at room temperature is sufficient to assemble a broad range of octahedrally coordinated [2]metallorotaxanes in excellent yields. The reactions have few, if any, by-products and proceed under thermodynamic control in the absence of a catalyst or any other external reagents.

Catenanes have previously been synthesized around octahedral metal templates by employing macrocycles containing tridentate 2,6-diiminopyridine chelating units.[7] This system is not well-suited to forming rotaxanes, however, because thread–thread–metal and macrocycle–macrocycle–metal (catenate) complexes can form in competition with the desired thread–macrocycle–metal assembly. Replacement of the macrocycle imine ligand set by nonlabile amine groups removes the possibility of forming catenates and introduces a structural asymmetry that can potentially be tailored to favor rotaxane formation under dynamic exchange conditions.[8]

After exploring several unsuccessful designs, we investigated the chemistry of macrocycle **L1**, which is conveniently prepared on a multigram scale in five steps from readily available materials (Scheme 1). The key step to **L1** is the macrocyclization of a bis-2-nitrobenzenesulfonamide (NsNH) derivative with 2,6-dibromomethylpyridine to give the protected macrocycle in 67% yield. Cyclization of the analogous Boc-protected diamine proceeded with a low yield (< 20%) and routes based on ring-closing olefin metathesis to form the C_{10} chain also proved uncompetitive. The use of aniline, rather than benzylamine, in the thread was designed to destabilize the dithread–metal complex with respect to the desired interlocked structure (see below).



Scheme 1. Five-component self-assembly of octahedral metal(II)[2]rotaxanes, [M(**L1L2**)]$(ClO_4)_2$. Reagents and conditions: a) 1,10-dibromodecane, K_2CO_3, NaI, butanone, reflux, 18 h, 83%, b) $LiAlH_4$, THF, 0–60°C, 3 h, 92%, c) 2-nitrobenzenesulfonyl chloride (NsCl), NEt_3, CH_2Cl_2, 18 h, 93%, d) 2,6-dibromomethylpyridine, K_2CO_3, butanone, reflux, 18 h, 67%, e) mercaptoacetic acid, LiOH, DMF, 24 h, 80%.

Octahedral metal–rotaxane formation was achieved by sequential treatment of **L1** with $Zn(ClO_4)_2 \cdot 6H_2O$ (0.8 equiv), 2,6-diformylpyridine (1 equiv) and (*p*-aminophenyl)tris(*p*-*tert*-butylphenyl)methane (2 equiv), Scheme 1. Remarkably, after 24 h at room temperature no metal-containing species other than the zinc(II)[2]rotaxane was evident by either ^1H NMR or electrospray mass spectrometry and the analytically pure [Zn(**L1L2**)]$(ClO_4)_2$ rotaxane was isolated in 92% yield by simply washing the crude product with diethyl ether. The generality of the reaction was explored by using divalent metal ions both across and down the periodic table with respect to zinc (i.e., Mn←Zn and Zn→Hg). Pleasingly, each of [M(**L1L2**)]$(ClO_4)_2$ (M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Hg^{II}) could be efficiently prepared by using the procedure in isolated yields ranging from 73 to 99% (Scheme 1). In all cases no other metal-containing species could be detected[9] after 24 h, which suggests near-quantitative formation of the interlocked metal-rotaxane complex. Formation of [Fe(**L1L2**)]$(ClO_4)_2$ required a longer reaction time and gentle heating (CH_2Cl_2/CH_3CN, N_2, 40°C, 2 weeks) and

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resulted in a lower yield of rotaxane (57 %). The sluggish rate of reaction is characteristic of the slow rate of ligand exchange of low spin d^6 metal complexes, but a potentially useful feature of the slower dynamics is that Fe^{II} therefore locks the rotaxane architecture in a particularly kinetically stable form.

The nonparamagnetic metal–rotaxane complexes all have similar ^1H NMR spectra; those of the zinc(II)[2]rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ and macrocycle **L1** are shown in Figure 1.[10] The shielding of the H_C and H_D protons of the benzyl rings of the macrocycle and several protons of the thread indicate that extensive intercomponent π stacking occurs in solution. Single crystals of $[Cd(\mathbf{L1L2})](ClO_4)_2$ suitable for investigation by X-ray crystallography were obtained by slow vapor diffusion of diethyl ether into a solution of the rotaxane in acetonitrile.[11] The crystal structure (Figure 2) confirms the interlocked molecular architecture, the pseudooctahedral geometry of the cadmium(II) ion, and shows π stacking of both the macrocycle benzylic rings with the pyridyl unit and an imine group of the thread.

The mechanism of the rotaxane-forming reaction provides insight into the reasons for the effectiveness of the ligand assembly. When **L1** is treated with $Zn(ClO_4)_2{\cdot}6H_2O$ (CH_2Cl_2/CH_3CN, room temperature) followed by the preformed thread, **L2**, electrospray mass spectrometry shows that within 10 minutes the thread has extracted the zinc(II) ion from the macrocycle to form the dithread complex, $[Zn(\mathbf{L2})_2](ClO_4)_2$ in > 95 % yield (Scheme 2). The $[Zn(\mathbf{L2})_2](ClO_4)_2$ species is then quantitatively converted to the rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ over 24 h.[12] Whilst the

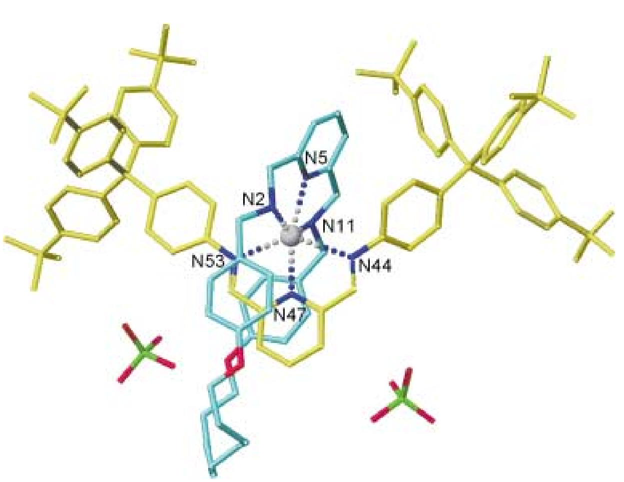


Figure 2. X-ray crystal structure of $[Cd(\mathbf{L1L2})](ClO_4)_2$.[11] Carbon atoms of the macrocycle, **L1**, are shown in light blue and those of the thread, **L2**, in yellow; oxygen atoms are red; nitrogen dark blue; chlorine green; cadmium grey. Hydrogen atoms and a molecule of acetonitrile are omitted for clarity. Selected bond lengths [Å]: Cd-N2 2.40, Cd-N5 2.30, Cd-N11 2.40, Cd-N44 2.52, Cd-N47 2.26, Cd-N53 2.38; other selected interatomic distances [Å]: N2-N11 4.52, N5-N47 4.52, N44-N53 4.59; ligand bite angles [°]: N2-Cd-N11 141.5, N44-Cd-N53 139.2.

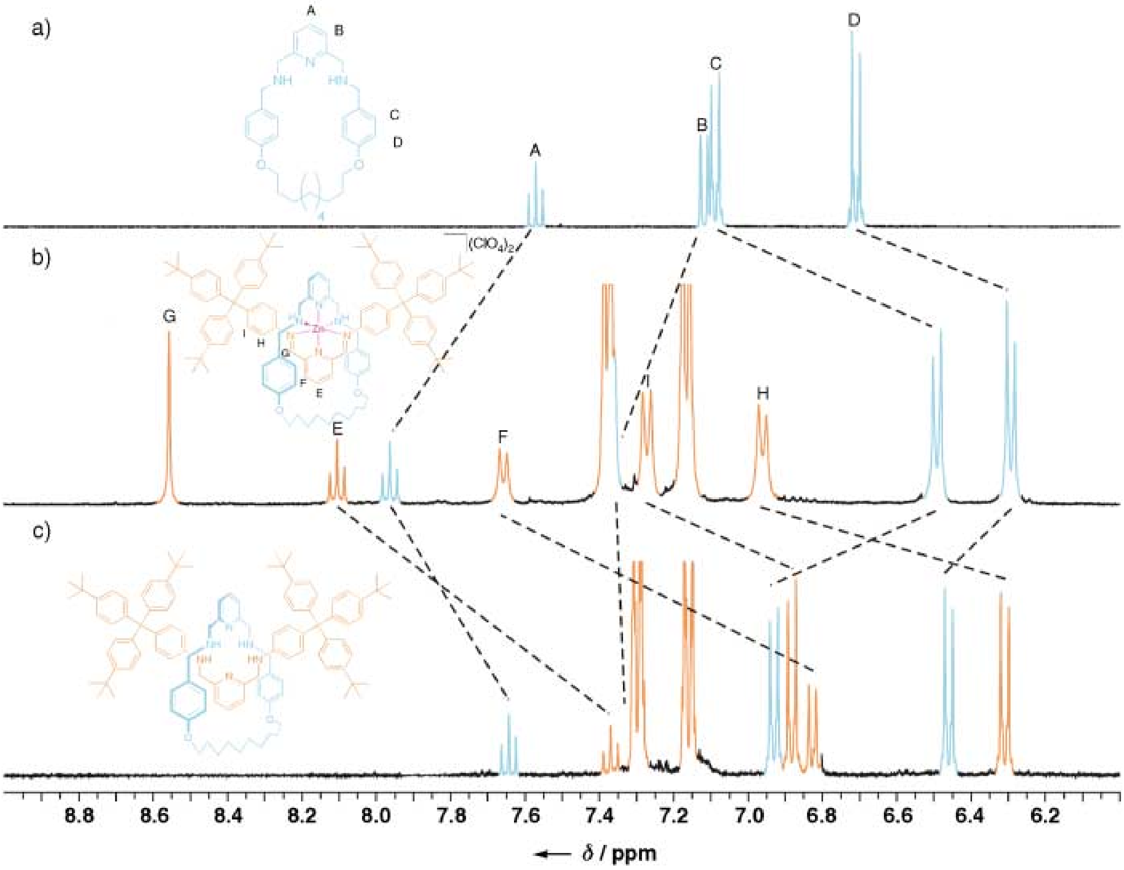
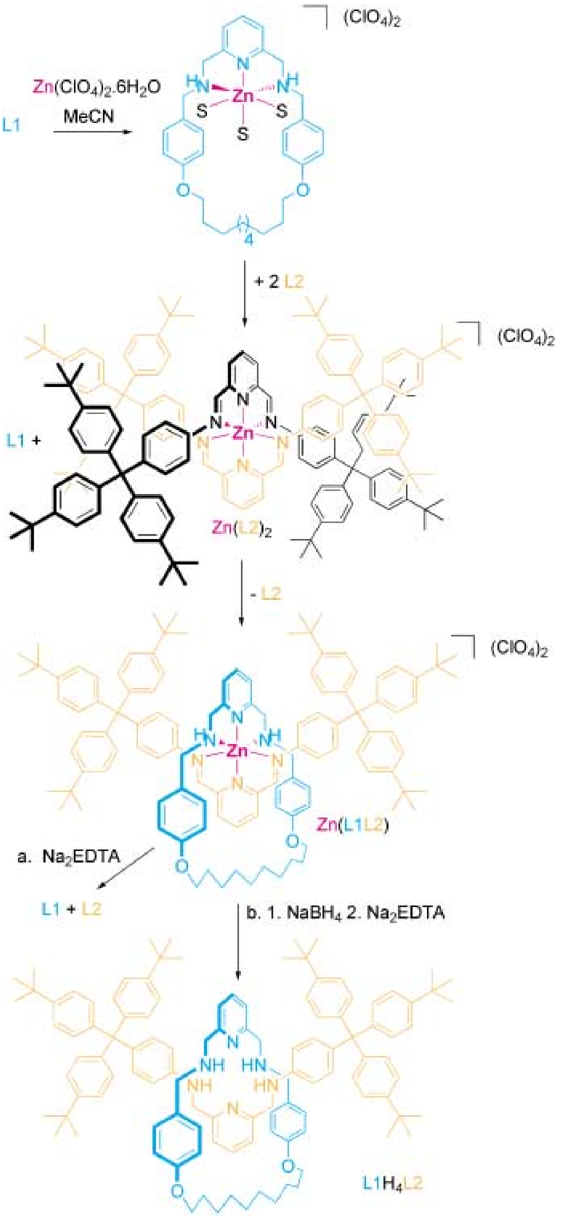


Figure 1. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298 K) of a) macrocycle **L1** b) zinc(II)[2]rotaxane $[Zn(\mathbf{L1L2})](ClO_4)_2$ c) demetallated, reduced, rotaxane $\mathbf{L1}H_4\mathbf{L2}$.



Scheme 2. Mechanism of formation and reactivity of [Zn(**L1L2**)](ClO$_4$)$_2$. Rapid formation of Zn(**L2**)$_2$ is followed by quantitative conversion to Zn(**L1L2**) under thermodynamic control. Demetallation of the rotaxane by using Na$_2$EDTA occurs both with (b) and without (a) prior reduction of the imine groups.

reversible nature of imine bond formation accounts for the dynamics of the system, the reasons for the metal–rotaxane complex being the thermodynamic product rather than the dithread–metal complex are rather more subtle. In fact, imine N donors often form stronger coordination bonds than the corresponding amines,[13] which leads to dithread–metal complexes being thermodynamically favored in other ligand systems we investigated. However, the use of aniline rather than, for example, benzylamine groups in the thread does not allow geometries in which the dithread–metal complex can form attractive intercomponent π-stacking interactions, such as those observed in the rotaxane between the benzyl groups of the macrocycle and the extended π system of the thread in both solution (NMR spectroscopy) and the solid state (X-ray crystal studies). We believe these favorable secondary interactions are important for the thermodynamic stability of the rotaxane over the other possible products of the reaction.

The 2,6-diminopyridyl motif imparts high kinetic stability in metal-coordinated interlocked structures. Tetraimine metal(II) catenates are not demetallated by Na$_2$EDTA (EDTA = ethylenediaminetetracetate), which required reduction to the more labile tetraamine catenates for the metal atom to be extracted.[7] The [M(**L1L2**)](ClO$_4$)$_2$ rotaxanes, which contain a combination of imine and amine N donors, do react with excess Na$_2$EDTA when heated (10 equiv, CH$_3$CN/MeOH, 60 °C, 0.5 h) to remove the metal. However, without the stabilization provided by metal coordination the rotaxane decomposes through imine bond exchange and only free macrocycle and thread are observed experimentally (Scheme 2, path a). If the rotaxane imine bonds are reduced beforehand ([Zn(**L1L2**)](ClO$_4$)$_2$, 10 equiv NaBH$_4$, CH$_3$CN/MeOH, Δ, 1.5 h), however, treatment with Na$_2$EDTA (10 equiv, CH$_3$CN/MeOH, 60 °C, 0.5 h) gives the demetallated, reduced, rotaxane **L1**H$_4$**L2** (88 % yield) with no evidence of dethreading (Scheme 2, path b). The ^{1}H NMR of **L1**H$_4$**L2** is shown in Figure 1 c. The downfield shift in the resonances of the benzyl groups with respect to [Zn(**L1L2**)](ClO$_4$)$_2$ indicates that π stacking with the thread is less pronounced in the demetallated rotaxane in which there are no coordination bonds to organize the geometry of the components.

In conclusion, we have developed a general ligand system for the efficient assembly of [2]rotaxanes around octahedral metal ions. The five component self-assembly reaction produces rotaxanes under true thermodynamic control in excellent yields without the need for large excesses of reagents, subsequent derivatization to stabilize the rotaxane architecture, chromatography or any other complicated purification processes. The system is remarkable in terms of its simplicity and expands both the range and geometry of metal ions that can be readily encapsulated within rotaxane structures.

Experimental Section

Typical example of octahedral metal(II)[2]rotaxane formation, [Zn(**L1L2**)](ClO$_4$)$_2$: Zinc(II) perchlorate hexahydrate (0.127 g, 0.342 mmol) in acetonitrile (5 mL), 2,6-pyridinedicarboxaldehyde (0.055 g, 0.410 mmol) in acetonitrile (10 mL), and *p*-aminophenyltris(*p-tert*-butylphenyl)methane (0.413 g, 0.820 mmol) in dichloromethane (10 mL) were added sequentially over five-minute periods to a solution of **L1** (0.200 g, 0.410 mmol) in acetonitrile (10 mL). The resulting solution was stirred at room temperature for 24 h, after which the solvent was removed under reduced pressure, the crude residue dissolved in acetonitrile (30 mL), filtered, and finally the solvent removed under reduced pressure. The crude residue was washed with diethyl ether (30 mL) for 10 min, isolated by filtration and dried in air to give [Zn(**L1L2**)](ClO$_4$)$_2$ as a bright yellow solid (0.582 g, yield = 92 %). Mp 266 °C (decomp). ^{1}H NMR (400 MHz, CD$_3$CN, 298 K): $\delta = 1.32$ (s, 54 H, C(CH$_3$)$_3$), 1.48–1.68 (bm, 12 H, alkyl), 1.79 (m, 4 H, OCH$_2$*CH$_2$*), 3.84 (br, 4 H, OCH$_2$), 4.06–4.55 (br, 8 H, pyC*H$_2$*NHC*H$_2$*Ar; py = pyridyl), 6.29 (d, $J = 8.6$ Hz, 4 H, macrocycle ArH), 6.49 (d, $J = 8.6$ Hz, 4 H, macrocycle ArH), 6.96 (d, $J = 8.6$ Hz, 4 H, thread ArH), 7.16 (d, $J = 8.6$ Hz, 12 H, thread ArH), 7.27

(d, $J = 8.6$ Hz, 4H, thread ArH), 7.37 (m, 14H, thread ArH plus macrocycle pyridyl H), 7.65 (d, $J = 7.8$ Hz, 2H, thread pyridyl H), 7.96 (t, $J = 7.8$ Hz, 1H, macrocycle pyridyl H), 8.11 (t, $J = 7.8$ Hz, 1H, thread pyridyl H), 8.57 ppm (s, 2H, thread HC=N); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): $\delta = 25.6$, 28.4, 28.5, 29.4, 31.5, 34.5, 52.2, 55.3, 63.9, 67.4, 114.1, 120.8, 123.0, 124.1, 124.3, 124.6, 127.0, 128.5, 130.6, 141.5, 141.9, 143.3, 143.4, 145.9, 148.9, 149.0, 155.0, 158.2, 158.7 ppm; IR (KBr pressed pellet): $\tilde{\nu} = 3465$, 2960, 2865, 1611, 1582, 1513, 1464, 1395, 1363, 1251, 1180, 1109, 1089, 1017, 840, 823, 637, 625, 582 cm^{-1}; LRESI-MS: $m/z = 830$ [Zn(**L1L2**)]$^{2+}$, 1759 [Zn(**L1L2**)](ClO_4)$^{+}$; HRFAB-MS (3-NOBA matrix): $m/z = 1657.97065$ (calcd for $^{12}C_{111}{}^{13}CH_{132}N_6O_2{}^{64}Zn$ [(**L1L2**)Zn], 1657.97363).

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Keywords: coordination modes · rotaxanes · self-assembly · template synthesis · thermodynamic control

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[9] Reactions were monitored by electrospray mass spectrometry in all cases and by ^{1}H NMR spectroscopy for systems not containing paramagnetic metals.

[10] The **L1** and **L2** resonances in [Zn(**L1L2**)](ClO_4)$_2$] were distinguished by a combination of COSY and ROESY experiments.

[11] [Cd(**L1L2**)](ClO_4)$_2$·2 MeCN·1.5 Et_2O: $C_{124}H_{153}CdCl_2N_8O_{11.5}$, $M_r = 2098.82$, yellow block, crystal size $0.15 \times 0.12 \times 0.10$ mm, monoclinic Cc, $a = 31.636(2)$, $b = 22.4269(14)$, $c = 22.2668(15)$ Å, $\beta = 133.7570(10)°$, $V = 11410.8(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.222$ Mg m^{-3}; $Mo_{K\alpha}$ radiation (graphite monochromator, $\lambda = 0.71073$ Å), $\mu = 0.300$ mm^{-1}, $T = 150(2)$ K. 36017 data (22989 unique, $R_{int} = 0.03170$, $1.27 < \theta < 28.96°$), were collected on a Bruker SMARTApex CCD diffractometer by using narrow frames (0.3° in ω), and were corrected semiempirically for absorption and incident beam decay. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELXTL manual, Siemens Analytical *X*-ray Instruments, Madison WI, USA, **1994**, version 5) to give $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1536$, conventional $R = 0.0627$ for F values of 22989 reflections with $F_o^2 > 2\sigma F_o^2$), $S = 1.048$ for 1371 parameters. Residual electron density extremes were 1.12 and -0.89 e Å^{-3}. Hydrogens were added in calculated positions and constrained to a Riding model. CCDC-224059 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] Under identical experimental conditions the reduced thread, H_4**L2**, does not afford [Zn(**L1**H_4**L2**)](ClO_4)$_2$, thus precluding the possibility of a "slippage" mechanism.

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