Transition-Metal-Complexed Cyclic [3]- and [4]Pseudorotaxanes Containing Rigid Ring-and-Filament Conjugates: Synthesis and Solution Studies

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Abstract: By using the "gathering-andthreading" effect of copper(I) with rigid ring-and-string conjugates, daisychain-type [3]- and [4]pseudorotaxanes could be prepared in high yields. The organic fragment used consisted of a 2,9-diphenyl-1,10-phenanthroline

(dpp)-containing ring attached to a coordinating filament capable of threading through the ring of another molecule by coordination to copper(I). The bidentate chelate introduced in the axis was also a 1,10-phenanthroline (phen) derivative with two methyl groups *ortho* to the nitrogen atoms of the phen unit. The organic component was prepared following a multistep strategy, one of the key steps being the attachment of the ring to the lateral axis. This connection was done by a condensation reaction between an *ortho* dione located at the back of a ring-incorporated phen and an aromatic aldehyde, which was the end-function of the thread. An oxazole nucleus was obtained after the condensation, which provided a rigid connection between the ring and the axis. In this way, the coordination axes of the ring-incorporated bidentate chelate and of the ligand belonging to the lateral filament were approximately orthogonal to one another. The design was such that the tetrameric complex, a [4]pseudorotaxane, seemed to be the most stable species, owing to the mutual geometrical arrangement of the filament and the ring. Various spectroscopic techniques, such as ¹H NMR spectroscopy,

Keywords: copper • multinuclear assemblies • rotaxanes • silver • template synthesis including DOSY, and electrospray ionization mass spectroscopy (ESI-MS), clearly demonstrated that a mixture of cyclic [3]- and [4]pseudorotaxane was obtained; the proportions of both components depended on concentration and temperature. Copper(I) was not the only metal center leading to the formation of cyclic pseudorotaxanes. A similar effect was observed with silver(I) as the templating metal: quantitative formation of threaded species was observed, with a higher proportion of trimer over tetramer than in the copper(I) case. Concentration and temperature effects were investigated for both series of CuI- and AgI-complexed threaded species showing that formation of the trimer was favored upon dilution or heating of the solution.

Introduction

In the very broad field of catenanes and rotaxanes,^[1–8] Stoddart and co-workers introduced the concept of "daisy chains" several years ago.^[9] These rotaxanes or pseudorotaxanes (i.e., unstoppered) consisted of identical subunits composed of a ring attached to a filament. In the assembly process leading to the desired daisy chain, each ring was thread-

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ed by the filament of another molecule, while each filament passed through the ring of the other molecule (for dimers) or of a third component (for more complex systems). In this way, various types of noncovalently assembled architectures could be obtained, either with a cyclic structure or as linear poly- or oligomers. Many examples of daisy chains have been reported, based on hydrogen bonding or those containing cyclodextrins.^[10,11] [2]Rotaxane dimers of the daisy-chain family have also been used as molecular-machine prototypes, mostly in relation to "molecular muscles", which are able to undergo contraction or elongation under the action of a given signal.^[12] Our group has been mostly interested in transition-metal-containing catenanes and rotaxanes^[13-16] and, in this context, the first rotaxane dimer of the daisychain family was made in 2000.^[17] This first hermaphroditic compound was used as a precursor for the synthesis of a molecular muscle, which could be set in motion by using a metal-exchange (Cu⁺/Zn²⁺) reaction.^[18] In view of expanding the family of compounds from rotaxane dimers to cyclic oligomers and also to prepare new molecular machines, the motion of which would be more complex than stretchingcontraction of a linear assembly, we deliberately introduced

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structural characteristics into the molecular fragments to be assembled that prevented formation of dimers. In this way, copper-complexed cyclic oligomers, namely, [2]pseudorotaxane tri- or tetramers, could be obtained.^[19]

Results and Discussion

Design: The construction principle of a hermaphroditic compound, the precursor of a molecular muscle,^[17] is represented in Figure 1. The assembly step is based on the forma-



Figure 1. The ring-and-filament conjugate incorporates two bidentate chelates of the 1,10-phenanthroline (phen) family represented by U-shaped symbols. The black dot is a metal center (copper(I)). For two organic components of the ring-and-filament-type to afford the two-metal complex depicted, significant folding is required, with the introduction of a kink in the filament or folding of the ring itself.

tion of nitrogen-containing, four-coordinate copper(I) complexes; each metal is complexed to two chelating groups. This situation corresponds to the most stable coordination mode of this d¹⁰ metal (tetrahedral or nearly tetrahedral geometry). It has been named the "gathering-and-threading" reaction due to the role of the copper(I) center, which brings the various components together and forces the stringlike fragments to thread through the rings. Since the coordination axes of the ring-incorporated chelate and the chelate that belongs to the thread have to lie approximately parallel to one another in the final dimer complex, the starting ring-and-filament conjugate has to be flexible so as to allow the ring and/or the string to fold up in the coordination process, as represented in Figure 1.

To prepare higher nuclearity [n]rotaxane or [n]pseudorotaxane complexes (n > 2), strict control over the geometry of the system is required, with particularly stiff ring-and-filament conjunctions. If the axes of the two coordination sites belonging to the ring and the thread can be maintained more or less orthogonal to one another, it will be impossible to form the dimer represented in Figure 1. Instead, a tetramer is likely to be formed. To exert strict geometrical control over arrangements formed by coordination of the two complexing units of the organic component to metal centers, it seems preferable to link the ring-contained chelate to the filament-incorporated chelating unit directly, as depicted in Figure 2.

If the two chelates of the same transition-metal complex are not perpendicular to each other, other structures can be expected, including, in particular, the cyclic tri- or pentamer. This is certainly the case for copper(I) complexes. Cu^{I} is a d^{10} metal and is thus not very demanding in terms of geometry. It can accommodate distorted tetrahedral geometries



Figure 2. Schematic representation of the organic component used for making [4]rotaxanes and the principle of the copper(I)-directed gathering-and-threading reaction; the black dot represents copper(I) and the U-shaped sign designates a bidentate chelate. Note that the linker between the back of the ring-included chelate and the chelate belonging to the thread has to be rigid for the 4-metal assembly to be obtained.

without substantial destabilization of the complexes, as already observed in many $[Cu(N-N)]^{2+}$ complexes^[20] (N-N: bidentate chelate of the phen family).

Synthesis of the ring-and-axis conjugate: Retrosynthetic analysis (Scheme 1) suggests that a condensation reaction of the macrocyclic dione^[21] with the linear phenanthroline-containing part terminated with an aldehyde function in the presence of ammonium acetate should provide the required rigid connection through a five-membered imidazole or oxazole ring (see below).



Scheme 1. Retrosynthetic analysis of ligand 9.

The synthesis of the linear part (Scheme 2) commenced with the preparation of 3,8-dibromo-1,10-phenanthroline^[22] (1). In the next step, monosubstitution of dibromide 1 by means of Suzuki coupling^[23] was carried out. The use of a slight excess of boronic acid 2 under catalysis by tetrakis(triphenylphosphine)palladium(0) allowed the isolation of the monosubstituted product 3 in 47% yield with recovery of unreacted starting material and disubstituted product. Then, the *p*-methoxyphenyl unit was attached by reaction of bromide 3 and boronic acid 4 under similar conditions as those described above; compound 5 was isolated in nearly quantitative yield.

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Scheme 2. Synthesis of ligand **9**. Reagents and conditions: i) $[Pd(Ph_3P)_4]$, Na_2CO_3 , toluene/H₂O, 47%; ii) $[Pd(Ph_3P)_4]$, Na_2CO_3 , toluene/H₂O, 92%; iii) 1) MeLi/toluene, 2) MnO₂, 3) MeLi/toluene, 4) MnO₂, 65%; iv) HCl/H₂O/dioxane, 83%; v) EtOH, 100°C, NH₄OAc, 59%.

Methyl groups were subsequently introduced on the 2and 9-positions of the phen moiety; the reaction was carried out in two repetitive two-step sequences, each one involving the addition of methyllithium followed by oxidation of the intermediate.^[22] The overall yield was 65%. Subsequently, the protective acetal group was hydrolyzed with diluted aqueous hydrochloric acid in dioxane to give aldehyde **7** in 83% yield.

In the last step of the synthesis, aldehyde **7** was reacted with the macrocyclic dione^[21] **8** in the presence of ammonium acetate. Usually, these reactions proceed well in acetic acid at reflux, yielding imidazole derivatives. In our case, a poorly soluble mixture of products, which proved difficult to separate, was obtained under such conditions. However, heating equimolar amounts of compounds **7** and **8** in the presence of ammonium acetate in ethanol in a pressure tube at 100 °C for 24 h afforded a mixture from which the main component was isolated in 59% yield and identified as oxazole derivative^[24] **9**. Thus, the synthesis of ligand **9** was accomplished in five steps starting from **1** and macrocyclic dione **8** was obtained in an overall yield of 14%. Ligand **9** showed limited stability when exposed to daylight in chloroform or dichloromethane. In the dark, however, it remained stable at room temperature for more than two weeks.

Copper and silver complexes: Preparation and characterization

Synthesis: Addition of an equimolar portion of [Cu-(CH₃CN)₄][PF₆] or Ag(OTf) (OTf=triflate) dissolved in CH₃CN to a suspension of **9** in CH₃CN under an argon atmosphere resulted in the formation of a brown–red solution in the case of Cu^I complexes and a yellow solution in the case of Ag^I complexes. The pseudorotaxanes formed, represented in Scheme 3, were characterized as described below.

ESI-MS studies of the copper-complexed pseudorotaxanes: Solutions of copper complexes in acetonitrile with concentrations of 10 and 0.01 mM (with respect to ligand 9) were allowed to equilibrate under argon for 24 h and submitted to MS analysis. Mass spectra were recorded by using the ESI method. At a concentration of 0.01 mM, only one significant signal at 1059.29 D with a spacing of isotope signals of around 0.3 D (Figure 3 a) corresponding to the formula [9+ Cu]₃³⁺ indicated the presence of trimeric species. At a concentration of 10 mM, two significant peaks above 1000 D were observed: one at 1059.32 D with a spacing of the isotope signals of about 0.25 D corresponding to the formula [9+Cu]₄⁴⁺ and the other at 1461.15 D with a spacing of around 0.33 D corresponding to the triply charged species [(9+Cu)₄PF₆]³⁺, both suggesting the presence of tetramers.

The ESI-MS experiments indicated that the size of oligomers depended on the concentration of ligand 9 and copper(I) cation. Therefore, tetra- and trimeric species were likely to be present in variable proportions at both concentrations investigated. To prove this hypothesis, we simulated superimposed isotope clusters of the mixtures of tetra-/ trimer at various molar ratios, assuming the relative abundance to be equal. We found that the simulated cluster of the mixture of tetra-/trimer of about 4:6 (Figure 3c) gave better agreement with the pattern experimentally observed at 0.01 mm (Figure 3a) than that of neat trimer (Figure 3b). For the 10 mm sample, a cluster simulated for the ratio of tetra-/trimer of about 7:3 (not shown) corresponded to the shape of the observed isotope signals. Hence, mass spectrometry analyses of the copper(I) complexes of ligand 9 revealed the presence of tetra- and trimeric species, the proportions of which depended on ligand 9 and copper(I) concentrations. At high concentration, the tetrameric complex



Scheme 3. Quantitative formation of Cu^I or Ag^I cyclic pseudorotaxanes in acetonitrile.



Figure 3. a) Isotope signals in the ESI-MS spectrum of the Cu^I complex recorded at a concentration of 10^{-5} M. b) Simulation of the isotope cluster corresponding to the pure trimer. c) Simulation of the isotope cluster corresponding to the tetramer/trimer (40:60) mixture.

appeared to dominate, whereas at low concentration the formation of trimeric species was favored.

NMR spectroscopy studies: The mass spectrometry study provided valuable information on the size (molecular weight) and composition of the oligomers formed upon complexation, whereas the cyclic structures attributed to Cu^I pseudorotaxanes (Scheme 3) were deduced from NMR spectroscopy results.^[19] We studied Cu^I and Ag^I complexes in greater detail by NMR spectroscopic methods to shed light on the subtle differences in their shape and size, manifested by differences in translational diffusion coefficients and also on their stereochemistry. We also investigated the dynamic interconversion between tri- and tetrameric species in solutions of both Cu^I and Ag^I complexes, in particular, the response of the systems to changes in concentration and temperature.

DOSY NMR spectroscopy: ¹H NMR spectra of the Cu¹ complexes recorded in CD₃CN at 5 mM (with respect to ligand **9**) revealed two sets of signals with intensity ratios of approximately 7:3. In accordance with the ESI MS study, the signals with larger intensities were attributed to tetrameric species $[9+Cu]_4^{4+}$, while the less intense peaks were assigned to trimeric species $[9+Cu]_3^{3+}$. Ag¹ complexes gave analogous spectra.

The assignment of a particular set of ¹H NMR spectroscopy signals to the particular cyclic n-mer was unequivocally confirmed by the DOSY NMR spectroscopy study. For the

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Table 1. Diffusion coefficients, D, in $\mu m^2 s^{-1}$ measured with DOSY experiments for the Cu^I- and Ag^I-complexed tri- and tetramer pseudorotaxanes.

	D for Cu ^I pseudorotaxane/PF ₆ ⁻	<i>D</i> for Ag ^I pseudorotaxane/OTf ⁻
trimer	380	390
tetramer	320	330

Cu^I complex, two different diffusion coefficients (*D*) were determined at 10 mm (Table 1). Higher diffusion coefficients, attributable to species of smaller volume, correlated with lower intensity signals, that is, supposed trimeric species (see above), whereas lower diffusion coefficients correlated with more intense signals, previously recognized as tetramers. This assignment is in full agreement with the preliminary ESI-MS-based study. The slightly higher values of *D* found for the Ag^I pseudorotaxanes can be explained by the smaller triflate counteranion associated with the Ag^I complexes compared with the hexafluorophosphate associated with Cu^I complexes.

Stereochemical analysis: Tetrahedral coordination of two nonidentical C_1 -symmetric bidentate chelates to a metal results in each metal center becoming stereogenic. Accordingly, the presence of diastereomers should be expected in the solution of tri- or tetramer complexes of ligand 9 and Cu^I. However, in the ¹H NMR spectrum of neat ligand 9, the protons of the phen units are only slightly asymmetrical in terms of their chemical shifts ($\delta \approx 0.1$ ppm). Thus, if the ligands form a tetranuclear complex by coordination to Cu¹, the phen groups coordinated to the metal centers in a tetrahedral manner create only a weakly inhomogeneous environment to one another. For example, proton H-4 (for numbering, see Scheme 3) of one ligand is equidistant from protons H-4' and H-7' of another ligand coordinated to the same metal center. However, the formation of the trimer brings about significant distortion of the dihedral angle formed by the planes of the coordinated phenanthrolines (to about 60°) and, consequently, the distance of H-4 to H-4' would be significantly different from that of H-4 to H-7'. This should create a more pronounced asymmetrical environment for each proton, resulting in larger separations of their NMR chemical shifts. The number of signals for each proton in the trimer could be predicted by stereochemical analysis (Figure 4).

"Homochiral" stereoisomers A and E are enantiomers. They represent an interesting example of cyclostereoisomerism.^[25] "Heterochiral" stereoisomers B, C, and D are indistinguishable and so are F, G, and H; these two groups of stereoisomers are also enantiomers. Hence, the total number of species distinguishable by NMR spectroscopy is reduced to two in a homo-/heterochiral ratio of 1:3. Whereas homochiral species exhibit a C_3 axis of symmetry and will produce only one set of signals with threefold intensity, the heterochiral species possess a C_1 axis, and should therefore give three sets of signals. Provided that homo- and heterochiral



Figure 4. Stereochemical analysis of the number of diastereomeric species for the trimer. Each vertex of the triangle represents a stereogenic copper(I) center.

species are thermodynamically equally stable, four sets of signals should be expected with overall ratio of intensities 1:1:1:1. However, the chemical shifts of protons of a particular ligand are likely to be more significantly influenced by the two stereogenic centers to which it is coordinated rather than by the remaining distant copper(I) center. Hence, depending on the measurement conditions, in particular, on the resolution of the NMR spectrometer, reduction of the total number of NMR-distinguishable species to three $(S \rightarrow$ R, $2 \times R \rightarrow R$, $R \rightarrow S$ and their respective enantiomers) with intensities of 1:2:1 can be expected. This is indeed observed for the ¹H NMR chemical shifts of protons H-7' and H-4' of the trimer. For example, the multiplet centered at $\delta =$ 9.21 ppm (H-7', Figure 5) consists of 3 doublets with intensities of 1:2:1. Centered at $\delta = 9.12$ ppm (H-4'), another such multiplet appears, which tends to separate even further into 4 doublets with intensities of 1:1:1:1. Similar multiplicities



Figure 5. Part of the ¹H NMR spectrum (600 MHz) of a mixture of Cu¹ tetra- and trimer in CD₃CN at concentration of 5×10^{-5} M.

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can be observed for several other aromatic protons located near the metal centers. In line with the above prediction, analogous peaks for tetrameric species (δ =9.27 for H-7'and 9.175 ppm for H-4') exhibit significantly lower separation.

Equilibrium studies: As evidenced by the above-presented studies, both Cu^I and Ag^I complexes of ligand **9** in acetonitrile consist almost solely of tri- and tetrameric cyclic pseudorotaxanes, the proportions of which depend on the total concentration of ligand **9** (further denoted as [L]) within the concentration range of 0.01 to 10 mM. These studies also revealed that concentration changes bring about interconversion between the two products with a slow rate with respect to the NMR timescale, allowing the analysis of the equilibrium between the tetra- and the trimeric species [Eq. (1); C₃ and C₄ stand for cyclic tri- and tetramer, respectively] by ¹H NMR spectroscopy.

$$4C_3 \rightleftharpoons 3C_4$$
 (1)

Despite the complexity of the NMR spectra, due to the presence of several diastereomers, equilibrium concentrations could be obtained by integration of the proton signals of the methoxy groups belonging to tri- and tetrameric species.^[19]

Two series of samples of Cu¹ and Ag¹ complexes were prepared by dilution of 10^{-2} M (based on [L]) stock solutions of mixtures of $[9+M]_4^{4+}$ and $[9+M]_3^{3+}$ complexes in deuterated acetonitrile at 298 K. These diluted samples in the concentration range of 10 to 0.05 mM were allowed to equilibrate under an inert atmosphere and their ¹H NMR spectra were recorded. Samples were measured in at least two subsequent time-shifted experiments to verify that equilibrium was attained. The yields of tri- and tetrameric species expressed in percentages^[26] were calculated and plotted (Figure 6) as a function of [L].

Inspection of the plots revealed that tetrameric pseudorotaxanes dominated in solution for both complexes over a wide range of concentrations; Cu^I complexes contained a larger proportion of tetrameric species than the Ag^I system. Plots for both Cu^I and Ag^I complexes in Figure 6 can be vertically dissected into two regions delineated by the concentration of ligand **9** at which it is equally distributed into triand tetrameric cycles ($[L]_{50}=0.2$ and 0.7 mM for copper and silver complexes, respectively). Below this concentration, the yield of trimers grows rapidly as [L] approaches infinite dilution.

The observation that Cu^{I} cations tend to shift the equilibrium towards tetrameric species more significantly than the Ag^I templates was quantified by the determination of the equilibrium constant, *K*, defined by Equation (1) for both systems. Rather than calculating single-point values of *K* for each [L] measured, a model function describing the relative proportion of trimeric species was developed (see Computational Methods in the Experimental Section) and fitted to experimental data by means of a least-squares method (Figure 6, solid lines) yielding estimates of the apparent



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Figure 6. Yields of tri- (triangles) and tetramers (squares) determined by ¹H NMR spectroscopy at various concentrations of ligand **9** [L]: a) Cu¹ complexes, b) Ag¹ complexes. Nonlinear regression of the yields of trimers were used for the calculation of estimates of equilibrium constants, *K*. [L]₅₀ represents the total concentration of ligand **9** at which the ligand is equally distributed in tri- and tetramers.

equilibrium constants of $K = (1.42 \pm 0.25 \times 10^4)$ and $(3.60 \pm 0.50 \times 10^3) \,\mathrm{M}^{-1}$ for Cu^I and Ag^I complexes, respectively.

In general, the major enthalpic contribution to the free energy change associated with the conversion of a cyclic oligomer, C_i , composed of *i* rigid ligands of **9** and metal cations M, to its larger homologue C_{i+1} is assumed to be dependent on the nature of the complexed metal and on its coordination sphere geometry, namely, the mutual arrangement of the two phen chelates (dihedral angles), and the M-N distances. Neglecting differences in solvation of the individual cyclic homologues, formation of a higher homologue should be accompanied by the loss of entropy arising from statistical effects, in particular, the loss of translational and rotational entropy upon formation of a lower number of species with higher molecular weight and higher symmetry. Specifically for the conversion of a cyclic trimer to a tetramer, the enthalpy contribution arising from the ideal tetrahedral arrangement of the phen ligands around the metal centers in

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the square-shaped tetramer, compared with the necessarily distorted one in the trimer, is assumed to be favorable. Thus, the formation of the tetramer is expected to be driven by enthalpy, whereas the reaction in the opposite direction should be entropy controlled.

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Variable-temperature measurements: The temperature dependence of the equilibrium composition was studied to give an insight into the origin of the driving forces, confirming or disproving the assumptions provided above. The ¹H NMR spectra of a mixture of Cu^I or Ag^I pseudorotaxanes in CD₃CN ([L]=0.01 and 0.005 M, respectively) were recorded at temperatures^[28] varying from 298 to 346 K (343 K for Ag^I complexes). The yields^[26] of tetra- and trimeric species were determined by integration of signals of the methoxy groups, as described above, and plotted against temperature (Figure 7). Upon heating, the equilibrium ratios of tetra- and trimeric pseudorotaxanes, involving either Cu^I or Ag^I templating cations, were shifted in favor of trimers.

In the case of Cu^{I} complexes (Figure 7 a), the tetramer is the major compound over the whole range of temperatures



Figure 7. Yields of tri- (triangles) and tetramers (squares) determined by ¹H NMR spectroscopy at various temperatures in solutions of complexes a) Cu¹ ([9]=0.01 M) and b) Ag¹ ([9]=0.005 M).

studied and the ratio of tri-/tetramer varies from 24/76 to 41/59. Ag^I complexes start with a ratio of tri-/tetramer of 35/65 at 298 K, which shifts in favor of the trimer as the temperature increases, the yield of both species becomes nearly identical at 343 K (Figure 7b).

The association constants calculated from the concentrations of the two pseudorotaxanes determined at each temperature were plotted against the reciprocal values of the temperature in conventional van 't Hoff plots ($R \ln K$ vs. 1/ T; Figure 8) for both systems. Assuming that ΔH° and ΔS°



Figure 8. *R* ln*K* versus 1/*T* data fitted with linear function y=ax+b, in which $a = -\Delta H^{\circ}$ and $b = \Delta S^{\circ}$; a) Cu¹ complexes, $\Delta H^{\circ} = -13100 \text{ cal } \text{m}^{-1}$, $\Delta S^{\circ} = -24.3 \text{ cal } \text{K}^{-1} \text{m}^{-1}$, r=0.99, and b) Ag¹ complexes, $\Delta H^{\circ} = -9526 \text{ cal } \text{m}^{-1}$, $\Delta S^{\circ} = -15.6 \text{ cal } \text{K}^{-1} \text{m}^{-1}$, r=0.97 (*r* is the correlation coefficient).

are independent of temperature in the measured range, the slopes and y intercepts obtained by linear regressions correspond to $-\Delta H^{\circ}$ and ΔS° , respectively. Negative values of ΔH° (-13.1 and -9.5 kcal m⁻¹ for copper and silver complexes, respectively) and $T\Delta S^{\circ}$ (-7.2 and -4.6 kcal m⁻¹ for copper and silver complexes, respectively; uncorrected for symmetry numbers) exhibited by both systems are consistent with the predictions of the driving forces provided above.

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Conclusion

Whereas in previous work dealing with hermaphroditic [2]rotaxane dimers and muscles a flexible organic component was used, the present study explores a rigid ring-andstring conjugate, for which the coordination axes of the ringand thread-incorporated bidentate chelates are approximately orthogonal to one another. This structural difference translated into dramatic consequences in terms of transitionmetal-induced formation of pseudorotaxanes: no dimer was observed but, rather, a mixture of tri- and tetramers was obtained with Cu^I or Ag^I as gathering-and-threading centers. The structures of tri- and tetrameric pseudorotaxanes were established by detailed MS and NMR spectroscopy studies. In particular, DOSY NMR spectroscopy measurements were informative and afforded the diffusion coefficients of the two species, allowing their unequivocal identification. Tetrameric pseudorotaxanes were favored at concentrations above 0.2 and 0.7 mm for copper and silver complexes, respectively, whereas below these concentrations the proportions of trimeric species increase rapidly with growing dilution. Equilibrium constants for the conversion of tri- to tetrameric species obtained from NMR spectroscopy concentration studies revealed a higher preference of Cu^I cations for the tetrameric arrangement than Ag^I. Variable-temperature NMR spectroscopy measurements shoved that the proportions of trimers increase with increasing temperature. van 't Hoff analyses of the data suggest that the formation of tetrameric species is an enthalpy-favored and entropy-disfavored process, whereas the opposite holds true for the formation of trimeric pseudorotaxanes. This interpretation is consistent with the virtual absence of cyclic pentamers, since their formation would be disfavored by both enthalpy and entropy. Thus, the proportions of tri- and tetramers can be directed by templating metals, concentrations, and temperatures. The present work paves the way for the preparation of transition-metal-containing multirotaxanes, which could be obtained by stoppering of the compounds derived from the presently described molecular systems. It should also allow for the elaboration of molecular machines with complex functions related to the cyclic nature of these multirotaxanes.

Experimental Section

Instrumentation: NMR spectra were acquired on either a Bruker AVANCE 500 (¹H at 500.1 MHz and ¹³C at 125.8 MHz) or a Bruker AVANCE 600 (¹H at 600.1 MHz and ¹³C at 150.9 MHz) spectrometer. The spectra were referenced to residual proton solvent references or carbon solvent references. Mass spectra were obtained by using a Bruker MicroTOF spectrometer or a Waters Micromass ZQ with electrospray (ES) ionization in positive mode. High-resolution mass spectra were obtained by using a Waters Q-Tof Micro instrument with ES ionization. UV/Vis spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with a 1 cm path cell; all measurements were made in dichloromethane.

Chromatographic supports: Thin-layer chromatography was performed by using glass sheets coated with silica. Column chromatography was car-

ried out on silica gel (Kieselgel 60, 0.063–0.200 mm, Merck). Automatic flash column chromatography was carried out on an Isco Combiflash Retrieve machine with pre-packed RediSep silica columns.

Solvents and chemicals: Some solvents were dried in the laboratory by distillation under argon over an appropriate drying agent: tetrahydrofuran and toluene under sodium/benzophenone; dichloromethane, acetone, and ethanol over CaH_2 ; triethylamine over KOH. All other anhydrous solvents used are commercially available ("analytical grade").

Compound 3: Compounds 1 (1.69 g, 5.0 mmol) and 2 (1.67 g, 5.5 mmol) were dissolved in degassed toluene (40 mL) in a Schlenk tube under an argon atmosphere and tetrakis(triphenylphosphine)palladium (274 mg, 0.237 mmol) was added. Then a degassed 2M aqueous solution of Na₂CO₃ (15 mL) was added and the solution was heated at 100 °C with stirring for 24 h under an argon atmosphere. The reaction mixture was allowed to cool to room temperature and then it was partitioned between CH2Cl2 (200 mL) and water (100 mL). The organic layer was washed with water (2×50 mL), dried with Na2SO4, and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, 120 g, CH_2Cl_2) to give **3** as a colorless powder (1.061 g, 47%). ¹H NMR (600.13 MHz, CDCl₃): $\delta = 9.41$ (d, J = 2.3, 1H), 9.19 (d, J =2.3 Hz, 1 H), 8.42 (d, J=2.3 Hz, 1 H), 8.38 (d, J=2.3 Hz, 1 H), 7.90 (d, J= 9.0 Hz, 1 H), 7.78 (m, 2 H), 7.75 (d, J = 9.0 Hz, 1 H), 7.70 (m, 2 H), 5.50 (s, 1H), 3.82 (dt, J(gem)=11.2 Hz, 2H), 3.71 (dm, J(gem)=11.2 Hz, 2H), 1.33 (s, 3H), 0.84 ppm (s, 3H); 13 C NMR (150.92 MHz, CDCl₃): $\delta =$ 151.3, 149.8, 144.9, 144.4, 138.9, 137.6, 137.5, 135.9, 133.5, 129.6, 128.5, 128.1, 127.5, 127.1, 125.9, 119.8, 101.2, 77.7, 30.3, 23.0, 21.9 ppm; MS (ESI): m/z: 471 [M+Na]⁺; elemental analysis calcd (%) for C24H21BrN2O2: C 64.15, H 4.71, N 6.23; found: C 63.92, H 4.58, N 6.07. Compound 5: Compound 3 (200 mg, 0.445 mmol), 4-methoxyphenyl boronic acid 4 (101.5 mg, 0.67 mmol), and tetrakis(triphenylphosphine) palladium (27 mg, 22 µmol) were suspended in degassed toluene (5 mL) in a Schlenk tube under an argon atmosphere. Then a degassed 2M aqueous solution of Na2CO3 (2 mL) was added and the solution was heated at 100 °C with stirring for 18 h. The reaction mixture was allowed to cool to room temperature and then it was partitioned between CH₂Cl₂ (20 mL) and water (10 mL). The organic layer was washed with water (2×10 mL), dried with Na2SO4, and concentrated under reduced pressure. The residue was purified by flash chromatography (Silicagel, 40 g, CH₂Cl₂) to give 5 as a slightly yellowish powder (195 mg, 92%). ¹H NMR $(500.13 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 9.42$ (d, J = 2.3 Hz, 1 H), 9.41 (d, J = 2.3 Hz, 1H), 8.39 (d, J=2.3 Hz, 1H), 8.35 (d, J=2.3 Hz, 1H), 7.90 (s, 2H), 7.80 (m, 2H), 7.74 (m, 2H), 7.70 (m, 2H), 7.09 (m, 2H), 5.50 (s, 1H), 3.90 (s, 3H), 3.82 (dt, J(gem)=11.2 Hz, 2H), 3.71 (dm, J(gem)=11.2 Hz, 2H), 1.33 (s, 3H), 0.84 ppm (s, 3H);¹³C NMR (125.77 MHz, CDCl₃): $\delta = 160.1$, 149.5, 149.4, 145.2, 144.6, 138.8, 138.1, 135.4, 135.4, 133.4, 132.6, 130.0, 128.7, 128.6, 128.3, 127.5, 127.1, 127.0, 127.1, 114.8, 101.3, 77.7, 55.5, 30.3, 23.1, 21.9 ppm; MS (ESI): m/z: 499 [M+Na]+; elemental analysis calcd (%) for C31H28N2O3: C 78.13, H 5.92, N 5.88; found: C 77.84, H 5.73, N 5.97

Compound 6: Compound 5 (180 mg, 0.378 mmol) was suspended in dry toluene (5 mL) under an argon atmosphere in a Schlenk tube. The mixture was cooled to 0-5°C and 1.6M solution of methyllithium in diethyl ether (0.7 mL, 1.12 mmol) was added dropwise within 10 min. The color of the reaction mixture turned deep purple. The mixture was allowed to react at 0-5°C for an additional 2 h. Then the reaction was quenched by the dropwise addition of water at 0-5°C with stirring. Afterwards, the toluene phase was washed with water (3 mL) and the aqueous layer was further extracted with toluene (3×2 mL). The organic layers were combined and dried with sodium sulfate. The filtered yellow solution in toluene was stirred and MnO2 (1.1 g) was added portionwise until the disappearance of the yellow color. The progress of the oxidation was monitored by TLC. The insoluble material was filtered off through a Celite layer, which was subsequently thoroughly washed with CH2Cl2. Evaporation of the combined solutions gave a product (169 mg) consisting of two monomethylated positional isomers. This material was dissolved in dry toluene (3 mL) and the addition of methyllithium (0.4 mL, 0.64 mmol) was repeated, followed by treatment with MnO₂ as described above. The resulting crude product (185 mg) was subjected to flash chromatography

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(silica gel, 40 g, CH₂Cl₂/MeOH 99:1) to give **6** as an amorphous white material (124 mg, 65% overall yield). ¹H NMR (500.13 MHz, CDCl₃): δ =8.04 (s, 1H), 8.01 (s, 1H), 7.74 (s, 2H), 7.655 (m, 2H), 7.48 (m, 2H), 7.40 (m, 2H), 7.04 (m, 2H), 5.505 (s, 1H), 3.90 (s, 3H), 3.83 (dt, *J*(gem) = 11.2 Hz, 2H), 3.72 (dm, *J*(gem) = 11.2 Hz, 2H), 2.90 (s, 3H), 2.86 (s, 3H), 1.35 (s, 3H), 0.84 ppm (s, 3H); ¹³C NMR (125.77 MHz, CDCl₃): δ = 159.3, ≈158.0, ≈157.6, ≈144.5, ≈144.0, ≈140.4, 138.0, ≈136.9, ≈136.8, 136.4, 133.4, 132.2, 130.4, 129.2, 127.2, 127.0, 126.4, 125.8, 125.7, 113.9, 101.5, 77.8, 55.3, 30.3, 23.0, 21.9, 25.2, 25.1 ppm; MS (FAB): *m/z*: 527 [*M*+Na]⁺; elemental analysis calcd (%) for C₃₃H₃₂N₂O₃: C 78.55, H 6.39, N 5.55; found: C 78.42, H 6.27, N 5.43.

Compound 7: Compound **6** (102 mg, 0.202 mmol) was dissolved in dioxane (2 mL) under argon atmosphere and a 1 M aqueous solution of HCl (2 mL) was added. The solution was heated at 80 °C for 15 h and cooled to room temperature. Then it was concentrated under reduced pressure to about one half of the volume and the remaining suspension was neutralized with NaHCO₃. The precipitate was collected and dried in vacuum to give **7** as a brown powder (70 mg, 83%). ¹H NMR (500.13 MHz, CDCl₃): $\delta = 10.13$ (s, 1H), 8.09 (s, 1H), 8.06 (s, 1H), 8.04 (m, 2H), 7.78 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.66 (m, 2H), 7.41 (m, 2H), 7.05 (m, 2H), 3.90 (s, 3H, OCH₃), 2.92 (s, 3H), 2.90 ppm (s, 3H); ¹³C NMR (125.77 MHz, CDCl₃): $\delta = 191.8$, 159.3, 158.1, 156.8, 146.2, ≈ 144.5 , ≈ 143.8 , 137.2, 136.5, 135.7, 135.6, 131.9, 130.4, 130.0, 129.9, 127.4, 126.9, 126.2, 125.6, 114.0, 55.4, 25.1 ppm; MG (ESI): m/z: 441 [M+Na]⁺; elemental analysis calcd (%) for C₂₈H₂₂N₂O₂: C 80.36, H 5.30, N 6.69; found: C 80.14, H 5.11, N 6.58.

Compound 9: Compounds 7 (15.0 mg, 0.0358 mmol) and 8 (21.4 mg, 0.0359 mmol) were dissolved in anhydrous ethanol (2.5 mL) in a pressure-resistant tube and ammonium acetate (27.6 mg, 0.358 mmol, freshly purified by sublimation) was added. The reaction mixture was briefly bubbled with argon, the pressure tube was closed, and heated with stirring at 100 °C for 24 h. Then it was evaporated, the residue was dissolved in chloroform, and charged onto a column (silica, 12×1 cm, prepared in chloroform). Gradient elution from chloroform to chloroform/methanol 97:3 afforded 9 as a yellowish solid (21 mg, 59%). ¹H NMR (500.13 MHz, CDCl₃): δ = 8.98 (d, J = 8.3, 1 H; H-7'), 8.72 (d, J = 8.3 Hz, 1H; H-4'), 8.52 (m, 2H; H-m₁), 8.46 (d, J = 8.9 Hz, 4H; H-o'), 8.21 (m, 3H; H-3',8',7), 8.08 (s, 1H; H-4), 7.80 (s, 1H; H-5,6), 7.71 (d, J=8.3 Hz, 2H; H-o₁), 7.42 (d, J=8.3 Hz, 2H; H-o₂), 7.21 (d, J=8.9 Hz, 4H; H-m'), 7.06 (d, J = 8.6 Hz, 2H; H-m₂), 4.36 (t, J = 5.4 Hz, 4H; H- α), 3.91 (s, 3H; H-OMe), 3.88 (t, J = 5.4 Hz, 4H; H- β), 3.74 (m, 12H; H- γ , δ , ϵ), 2.99 (s, 3H; H-g), 2.94 ppm (s, 3H; H-h); 13 C NMR (125.77 MHz, CDCl₃): $\delta =$ $163.0,\ 160.4,\ 160.2,\ 159.4,\ 158.0,\ 157.1,\ 155.9,\ 155.8,\ 144.7,\ 144.6,\ 144.0,$ 143.7, 142.9, 137.0, 136.5, 136.4, 136.0, 134.7, 132.7, 132.4, 132.1, 131.5, 130.4, 130.0, 129.4, 129.0, 128.9, 127.4, 127.4, 127.0, 126.6, 126.1, 125.6, 121.4, 119.6, 119.4, 116.3, 115.68, 115.65, 114.0, 71.3, 70.8, 70.6, 69.6, 67.9, 55.4, 25.3, 25.3 ppm; MS (ESI): m/z: 1020 [M+Na]+; elemental analysis calcd (%) for C₆₂H₅₃N₅O₈: C 74.76, H 5.36, N 7.03; found: C 74.48, H 5.18, N 6.87.

Copper(I) complexes: Compound **9** (10 mg, 0.01 mmol, 1 equiv) was introduced in a degassed round-bottomed flask and degassed CD₃CN (0.6 mL) was added by using a syringe. Then a degassed solution of [Cu-(CH₃CN)₄][PF₆](3.7 mg, 1.00×10^{-5} mol, 1 equiv) in CD₃CN (0.4 mL) was introduced with a syringe (total concentration of compound **9**= 10^{-2} M). The brown-red color became darker as the ligand dissolved. The progress of the threading reaction was followed by TLC and there was no remaining starting material after 1 h. NMR spectroscopy samples were prepared with the following concentrations: 10^{-2} , 5×10^{-3} , 10^{-3} , and 10^{-4} M. The mixture of [**9**+Cu]₃·3PF₆ and [**9**+Cu]₄·4PF₆ was obtained quantitatively. For Cu¹ complexes: ¹H NMR data was published in our preliminary communication; $^{[19]}$ DOSY: diffusion coefficients values were 380 µm²s⁻¹ for [**9**+Cu]₃·3PF₆ and 320 µm²s⁻¹ for [**9**+Cu]₄·4PF₆ in CD₃CN, at 298 K and $C=10^{-2}$ M; UV/Vis: $\lambda(^{3}$ MLCT)=449 nm; MS (ESI): *m/z*: calcd for [C₁₈₆H₁₅₉N₁₅O₂₄Cu₃]³⁺: 1059.32; found: 1059.29; calcd for [C₂₄₈H₂₁₁₂N₂₀O₃₂Cu₄]⁴⁺: 1059.32; found: 1059.32.

Silver(I) complexes: Compound 9 (10 mg, 0.01 mmol, 1 equiv) was introduced in a degassed round-bottomed flask and degassed CD_3CN (0.6 mL) was added by using a syringe. Then a degassed suspension of

Ag(OTf) (2.6 mg, 1.00×10^{-5} mol, 1 equiv) in CD₃CN (0.4 mL) was introduced with a syringe (total concentration of compound $9 = 10^{-2}$ M). The fluorescence of the solution disappeared as the ligand dissolved. The progress of the threading reaction was followed by TLC and there was no remaining starting material after 2 h. Four NMR spectroscopy samples were prepared with the following concentrations: 10^{-2} , 5×10^{-3} , 10^{-3} , and 10⁻⁴ M. The mixture of [9+Ag]₃·3 OTf and [9+Ag]₄·4 OTf was obtained quantitatively. For Ag^I complexes: ¹H NMR (500.13 MHz, $c = 5.10^{-3}$ M in CD₃CN, the temperature of acquisition was 346 K, so the proportion of trimer (t)/tetramer (T) was modified to t/T = 51/49; the proportion was determined by using the integration of the methoxy group signal). ¹H NMR: $\delta = 9.25$ (d, J = 8.5 Hz, 1H; H-7'T), 9.19 (m, 1H; H-7't), 9.11 (d, J=8.5 Hz, 1H; H-4'T), 9.06 (m, 1H; H-4't), 8.94 (s, 1H; H-7t), 8.71 (s, 1H; H-7T), 8.64 (s, 1H; H-4T), 8.63 (m, 2H; H-m₁T), 8.54 (d, J =8.0 Hz, 2H; H-m₁t), 8.47 (s, 1H; H-4t), 8.35 (m, 2H; H-3',8't), 8.30 (m, 2H; H-3',8'T), 8.26 (s, 1H; H-5T), 8.25 (s, 1H; H-6T), 8.06 (s, 1H; H-5t), 8.05 (s, 1H; H-6t), 7.82 (d, J=8.0 Hz, 2H; H-o₁T), 7.77 (m, 2H; H-o'T), 7.70 (m, 6H; H-o₁,o't), 7.61 (d, J=8.0 Hz, 2H; H-o₂t), 7.50 (d, J=8.5 Hz, 2H; H-o₂T), 7.17 (d, J=8.5 Hz, 2H; H-m₂t), 7.13 (d, J=9.0 Hz, 2H; Hm₂T), 6.29 (m, 8H; H-m'T,m't), 3.94 (s, 3H; H-OMet), 3.91 (s, 3H; H-OMeT), 3.69–3.25 (m, 40H; H- α , β , γ , δ , ϵ t and T), 2.60 (s, 3H; H-gt), 2.48 ppm (s, 3H; H-gT); $\delta = 2.44$ ppm (s, 3H; H-hT); DOSY: diffusion coefficients values were 390 μ m²s⁻¹ for [9+Ag]₃·3 OTf and 330 μ m²s⁻¹ for $[9+Ag]_4$ + 4 OTf in CD₃CN, at 298 K and C=5.10⁻³ M; MS (ESI): m/z: calcd for [C186H159N15O24Ag3]3+: 1103.96, found 1104.16; calcd for $[C_{248}H_{212}N_{20}O_{32}Ag_4]^{4+}$ CF₃SO₃: 1521.71; found 1521.64.

Computational methods: The equilibrium constant defined by Equation (1) was expressed in terms of concentrations [Eq. (2)], in which $[C_4]$ and $[C_3]$ represent equilibrium concentrations of the tetrameric and trimeric cyclic complexes, respectively.

$$K = [C_4]^3 / [C_3]^4$$
(2)

Combining Equation (2) and the mass balance equation [Eq. (3)] allows the dependence of the concentration of the trimeric species $[C_3]$ on [L]and the equilibrium constant, *K*, to be expressed [Eq. (4); [L] stands for the total concentration of ligand **9**].

$$4[C_4] + 3[C_3] = [L] \tag{3}$$

$$[C_3] = \sqrt[4]{\frac{\left(\frac{|L|-3|C_3|}{4}\right)^3}{K}}$$
(4)

$$y = 300[C_3]/[L]$$
 (5)

A unique algebraic solution of Equation (4) for $[C_3]$ was found by using the Derive 6 program (Texas Instruments) under the constraints $K \in (0, \infty)$; $[C_3] \in [0, 1]$; $[L] \in [0, 1]$, and implemented in the Origin 7 program (OriginLab) in the form of Equation (5) (to fit the percentage yields of the trimeric species with *K* as a fitting parameter) as a user-defined function. The fitting function was then tested by using exact-fit data generated with Equation (4) and the Derive 6 program for arbitrarily chosen values of *K*, [L]. Subsequently it was used for fitting the percentage yields of the trimeric species (Figure 6) experimentally determined in mixtures of Cu¹ and Ag¹ complexes.

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