Neutral interlocked assemblies from anionic pseudorotaxanes coordinated to Sn(IV) and Cu(I) metallic centers

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Abstract

Anionic [2]pseudorotaxanes have been prepared by threading an axle consisting of two dithiophosphonate donor groups attached to a 1,4,5,8-naphthalenediimide (NDI) core through the cavity of the bis-1,5-(dinaphtho)-38-crown-10 ether (15DN38C10). The subsequent coordination of these interlocked, negatively charged species to R_3SnCl ($R = Me, Ph$) and $(Ph_3P)_2CuNO_3$ yields neutral (pseudo)rotaxanes of the general formula $NDI[(CH_2CH_2O)_n(An)PS_2^-\text{"M"}]_2 \subset 15DN38C10$ ($n = 1, 2$; $An = anisole$; $\text{"M"} = R_3Sn$ or $(Ph_3P)_2Cu$). Solution and solid state studies of the rotaxanation process show that there are two factors influencing the interaction between the axles and the wheel: the *size* of the stopper and the *length* of the side-arms of the axles. When the axle termini are bulky enough to prevent threading, the length of the side-arms has little influence over the self-assembly process. In contrast, when the size of the stopper does not preclude the threading of the axle through the cavity of the crown, the length of the side-arms is the determining factor in the rotaxanation process. These results presented here provide an alternative method for the synthesis of counter-ion free interlocked species, based on *anionic axles* with donor capabilities that would produce a neutral interlocked architecture upon threading and coordination to *cationic metal-containing centers*.

Keywords:

Pseudorotaxanes; Supramolecular chemistry; X-ray crystal structures; Phosphor-1,1-dithiolates; Metal complexes.

1. Introduction

The last decades witnessed an increased interest in the synthesis and characterization of molecular machines and devices based on mechanically interlocked molecules [1]. These species are composed of two or more distinct components connected in such a way that their dissociation is not possible without breaking one (or more) of their covalent bonds. Examples of such architectures include rotaxanes, catenanes, knots, and suitanes [1, 2]. Among these, rotaxanes are heavily studied, since the position of one component relative to the other can be controlled *via* various external inputs (photons, electrons, protons or chemicals) [3]. Pseudorotaxanes and rotaxanes consist of one or more macrocycles threaded into one or more axles (linear, dumbbell shaped molecules). Pseudorotaxanes are compounds that exist in equilibrium with their unthreaded counterparts (the macrocyclic component is free to slip off of the axle); in contrast, rotaxanes are interlocked compounds in which the crown is permanently trapped onto the axle by bulky stoppers at the axle termini [4-9].

The formation of (pseudo)rotaxanes depends on the presence of complementary recognition sites on both the axle and wheel. As extensively demonstrated by Stoddart [3a, 4] and others [5], a secondary dialkyl-ammonium center (Scheme 1a) can be used as a recognition site because it threads into crown ethers like dibenzo-24-crown-8 (DB24C8) and bis-*p*-phenylene-34-crown-10 (BPP34C10) with the formation of (pseudo)rotaxanes. Another set is based on the bis(pyridinium)ethane dication (Scheme 1b) and DB24C8, template that was used by Loeb to prepare a large variety of pseudo(rotaxanes) [6]. The threading of viologen species (Scheme 1c) through the cavities of crown ethers such BPP34C10 and bis-1,5-(dinaphtho)-38-crown-10 (15DN38C10) to form [(viologen)C(crown ether)]²⁺ [2] pseudorotaxanes has been studied by Stoddart [7] and others [8] and lies at the foundation of a wide range of mechanically interlocked molecules in general, and pseudorotaxane and rotaxane systems, in particular. Rotaxanes and pseudorotaxanes can also form from the naphthalenediimide π -deficient group (Scheme 1d) and the π -rich 15DN38C10 crown ether, as demonstrated by Sanders [9].

Scheme 1. Crown ethers and axle components used in the preparation of pseudorotaxanes and rotaxanes.

An important research direction in this field is the use of pseudorotaxanes as ligands. It is believed that the incorporation of metals within interlocked architectures would lead to a synergistic effect, thus enhancing the properties of the resulting species. As such, several metal-containing interlocked architectures have been prepared and characterized [6a,b, 8d-f, 9a, 10]. Usually, their design is based on

an axle having a recognition site for pseudorotaxane formation and equipped with donor groups for subsequent coordination to metallic centers. The resulting species could provide a blueprint for the future organization of more complex species into higher-order arrays, thus generating crystalline materials comprised of interlocked molecular components that could be independently manipulated [6a, b].

Despite the advances in this field, the rational synthesis of metal-based interlocked architectures still remains a challenging issue in synthetic chemistry. This situation stems from the fact that, while several complementary recognition sites could be used in the template-based synthesis of a “rota-ligand”, not all of them are robust enough to withstand the ensuing coordination process, which often requires either strongly donating polar solvents that disrupt the non-covalent interactions holding the pseudorotaxane together, or elevated temperatures. In addition, both pseudorotaxanes and metallic centers are frequently accompanied by counter-ions that often interfere with either the self-assembly process, or with the desired properties of these species.

An elegant strategy toward counter-ion free metal-based interlocked architectures was developed by Loeb [11], employing *zwitterionic pseudorotaxanes* as ligands and connecting them to *neutral metallic centers*. Mezei showed that neutral bimetallic pseudorotaxanes can also be obtained from the interaction between *positively charged pseudorotaxanes* (2+) and two *anionic* (1-) *metallic nodes* [8d,e].

We propose here an alternative method for the synthesis of these counter-ion free species, based on *anionic axles* with donor capabilities that would produce a neutral species upon threading and coordination to *cationic metal-containing centers*.

Recently, we have described the synthesis and characterization of two new ditopic ligands having dithiophosphonate donor groups linked to a 1,4,5,8-naphthalenediimide (**NDI**) core through ether spacers of different length (**1**-[NH₄]₂, Scheme 2) [12]. The reaction of these ligands with Ph₃SnCl and (PPh₃)₂CuNO₃ produced bimetallic complexes, of the general formula **2**-[M]₂, also depicted in Scheme 2. Structural investigations of these compounds revealed that the different length of the ligand's side-arms influence the relative position of the -(An)PS₂[M] groups (An = anisole) with respect to the central **NDI** moiety: a short side-arm (compounds of type **2a** in Scheme 2) places the -(An)PS₂[M] moiety in close proximity of the **NDI** group, while a longer side-arm (compounds of type **2b** in Scheme 2) directs the metallic centers away from the **NDI** moiety, thus influencing their molecular and supramolecular structures.

Scheme 2. Structural description of ditopic dithiophosphonate ligands and their metal complexes.

It is in this context that we decided to investigate the formation of anionic pseudorotaxanes using our **NDI**-based dithiophosphonate ligands **1**-[NH₄]₂ in combination with **15DN38C10**, and to explore their propensity to form neutral interlocked species upon coordination to metallic centers. We have also looked

at the interaction of the neutral **2**-[**M**]₂ complexes with the same crown ether, to ascertain which metallic group would act as a stopper for the crown and which would allow the crown to slip off of the axle component (rotaxane formation vs. pseudorotaxane formation). The results of our investigations are reported in this contribution.

2. Results and discussion

2.1. Strategy and syntheses

As a general strategy, to build anionic pseudorotaxanes that could also act as ligands, one would need a recognition motif that would not be affected by the presence of donor groups within the body of the rota-ligands. Since an anionic axle is soluble only in polar solvents, the use of recognition motifs based on hydrogen bonds would have limited success, as polar solvents interfere with the hydrogen bonds between the axle and the wheel. With these restrictions in mind, we decided to explore a π - π stacking based template, since these interactions are not affected by the presence of donor Lewis bases and are known to form even in polar solvents. As such, we have chosen **15DN38C10** ether (**3**) as wheel, because of its well-known π -electron donating capabilities toward various π -electron deficient substrates [9].

On another hand, dithiophosphonate-based ligands [(RO)R'PS₂][−] are known for their rich coordination chemistry: the presence of soft Lewis acidic centers on these ligands, *i.e.* sulfur, opens the possibility of supramolecular association through secondary bonds [13]. As such, combining this donor set with the π -deficient **NDI** moiety should produce an axle with a strong affinity for the **15DN38C10** wheel, with the added benefit of the versatility of the dithiophosphonate ligand.

The ditopic dithiophosphonate axles were synthesized as reported earlier [12], by the reaction of 1,4,5,8-naphthalene-tetracarboxylic dianhydride with two equivalents of either 2-aminoethanol or 2-(2-aminoethoxy)ethanol in DMF, followed by the reaction of the resulting diols with Lawesson's Reagent in benzene. The ammonium salts NDI[(CH₂CH₂O)_n(An)PS₂NH₄]₂ (n = 1: **1a**-[NH₄]₂; n = 2: **1b**-[NH₄]₂) were precipitated by passing dry gaseous NH₃ through the cold benzene solution of the dithiophosphonic acids. The axles coordinate to R₃SnCl (R = Me, Ph) or (Ph₃P)₂CuNO₃ (Scheme 2), yielding the bimetallic compounds **2a**-[SnMe₃]₂; **2a**-[SnPh₃]₂; **2a**-[Cu(PPh₃)₂]₂ (for n = 1) and **2b**-[SnMe₃]₂; **2b**-[SnPh₃]₂; **2b**-[Cu(PPh₃)₂]₂ (for n = 2). The molecular and supramolecular structures of **2a**-[SnPh₃]₂, **2a**-[Cu(PPh₃)₂]₂ and **2b**-[SnPh₃]₂ were described elsewhere [12]; their general structural characteristics feature the -PS₂ group coordinated in an either mono- (**2a**-[SnPh₃]₂ and **2b**-[SnPh₃]₂) or bidentate fashion (**2a**-[Cu(PPh₃)₂]₂). The most important structural differences, arising from the different length of the ligand's side arms, is the position of the (An)PS₂[**M**] groups with respect to the central **NDI** moiety: in **2a**-[SnPh₃]₂ and **2a**-[Cu(PPh₃)₂]₂ they virtually surround the **NDI** group, while in **2b**-[SnPh₃]₂ they are positioned away from the **NDI** moiety.

To gain insight into the rotaxation process involving these species, two routes toward neutral bimetallic interlocked architectures were investigated, Scheme 3. Path I involves anionic pseudorotaxane ligand formation as a first step, followed by coordination of the preformed "rota-ligand" to metallic centers. This investigation would afford information on the stability of the anionic pseudorotaxanes, as well as on their coordination behavior towards metallic centers. Path II is based on the slippage of the crown onto the preformed neutral metallic axles. Employing metallic centers with various additional ligands of different sizes, it is possible to establish which metallic group would allow the crown to be threaded by the bimetallic axle, and which would block the rotaxation process. Applying this

information to route I, one could obtain (depending on the size of the axle termini) either rotaxanes or pseudorotaxanes.

Scheme 3. Two synthetic pathways toward neutral bimetallic pseudorotaxanes starting from anionic axles; also given is the proton labelling mode used in NMR studies.

2.2. Solution Studies

Upon mixing equimolar solutions of axles **1a**-[NH₄]₂ or **1b**-[NH₄]₂ and **15DN38C10** (**3**) in acetone-d₆ : D₂O (5 : 0.6, v/v; the water is needed to help dissolving the anionic axle), the slow rate of association and dissociation of the components on the NMR timescale at room temperature permits the observation of three different sets of peaks in their NMR spectra (Fig. 1), corresponding to the free axles and crown ether, and the [2]pseudorotaxane species. The pseudorotaxane formation is indicated by the upfield shift of the NDI (H_a) and the crown aromatic peaks (H_{d-f}) due to aromatic shielding effects resulting from the NDI-crown interaction, while the anisole peaks (H_{b-c}) shifted downfield, indicative of an “outer sphere” interaction of this group with the crown **3** (for proton labeling mode see also Scheme 3).

Fig. 1. Partial ^1H -NMR spectra of a) crown **3**, b) axle **1a**- $[\text{NH}_4]_2$, c) pseudorotaxane **1a**- $[\text{NH}_4]_2 \subset \mathbf{3}$, d) pseudorotaxane **1a**- $[\text{NH}_4]_2 \subset \mathbf{3}$ / excess NH_4^+ , e) axle **1b**- $[\text{NH}_4]_2$, f) pseudorotaxane **1b**- $[\text{NH}_4]_2 \subset \mathbf{3}$ and g) pseudorotaxane **1b**- $[\text{NH}_4]_2 \subset \mathbf{3}$ / excess NH_4^+ ; H and H' represent protons bound to uncomplexed and complexed species, respectively (for proton labeling mode see Scheme 3); the peak at 7.33 ppm (marked with *) is C_6H_6 carried on from the synthesis of the axles.

The observation of signals for the resonances of threaded and unthreaded species in the NMR spectra of **1a**- $[\text{NH}_4]_2$ or **1b**- $[\text{NH}_4]_2$ and **3** allows the measurement of their association constants (K_a) and free energies of complexation (ΔG°) (Table 1) using the convenient single-point method [4a]. It should be noted that, since the NH_4^+ ion forms inclusion compounds with a large variety of crown ethers, the apparent K_a values reported here for pseudorotaxanes **1a/b**- $[\text{NH}_4]_2 \subset \mathbf{3}$ were calculated considering a 1 : 1 reaction of the anionic axles with the $[\mathbf{3} \cdot \text{NH}_4]^+$ inclusion complex. To avoid the formation of this undesired inclusion complex, we attempted to neutralize the dithiophosphonic acids using Me_4NOH and $n\text{-Bu}_4\text{NOH}$ as bases, instead of gaseous ammonia. Unfortunately, we observed decomposition of the axles in all cases. Anion exchange using R_4NCl ($\text{R} = \text{Me}$, $n\text{-Pr}$ and $n\text{-Bu}$) also failed. To the best of our knowledge, there is no information on the interaction between the NH_4^+ cation and **15DN38C10** and their complexation ratio. Comparing the available information on the association of NH_4^+ cation with crown ethers of similar size [14], we expected a 1 : 1 $[\text{NH}_4 \cdot \mathbf{3}]^+$ compound, although a 2 : 1 ratio cannot be ruled out *a priori*. To study the $\text{NH}_4^+ : \mathbf{3}$ complexation ratio, we performed an ESI^+/MS experiment onto a 5 : 1 mixture of NH_4PF_6 and **15DN38C10**. Analysing the spectrum, we have observed the base peak at 654 m/z corresponding to the 1 : 1 $[\text{NH}_4 \cdot \mathbf{3}]^+$ inclusion complex. There are three more peaks present, corresponding to the 1 : 1 $[\text{H} \cdot \mathbf{3}]^+$ (637 m/z, 50 %), 1 : 1 $[\text{Na} \cdot \mathbf{3}]^+$ (659 m/z, 10 %), and 1 : 1 $[\text{K} \cdot \mathbf{3}]^+$ (675 m/z, 4 %) inclusion complexes, respectively. Importantly, there is no peak at 336 m/z that would correspond to a 2 : 1 $[(\text{NH}_4)_2 \cdot \mathbf{3}]^{2+}$ inclusion complex. Since the dissolution of the axle produces two equivalents of NH_4^+

ions, it is reasonable to assume that in our experiments the formation of the $[\text{NH}_4\cdot\mathbf{3}]^+$ complex is essentially complete.

It is also conceivable that both NH_4^+ cations and **NDI**-based axles compete for the formation of the $[\text{NH}_4\cdot\mathbf{3}]^+$ inclusion complex and $\mathbf{1a/b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$ pseudorotaxanes, respectively. As such, when the NMR spectra of the axles $\mathbf{1a/b}\cdot[\text{NH}_4]$ and **15DN38C10** were recorded in the presence of excess NH_4PF_6 (Fig. 1 d and g), a small decrease of the K_a values was observed (Table 1). VT-NMR studies also showed that the overall concentration of the interlocked species increases with decreasing the temperature, as shown in Fig. 2 for $\mathbf{1b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$, either in the absence or presence of excess NH_4^+ .

Fig. 2. ^1H -VT-NMR (acetone- d_6 / D_2O , 5:0.6 v/v) of $\mathbf{1b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$, (top), and $\mathbf{1b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$ with excess NH_4PF_6 (bottom).

Addition of two equivalents of R_3SnCl ($\text{R} = \text{Me}, \text{Ph}$) or $(\text{Ph}_3\text{P})_2\text{CuNO}_3$ to pseudorotaxanes $\mathbf{1a/b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$ (path I) resulted in the formation of mixtures of unthreaded bimetallic axles and bimetallic pseudorotaxanes. Unfortunately, the only species soluble in this solvent system (acetone/ H_2O , 5:0.6 v/v) are the $\mathbf{2b}\cdot[\text{SnMe}_3]_2 \subset \mathbf{3}$ pseudorotaxane and its corresponding unthreaded $\mathbf{2b}\cdot[\text{SnMe}_3]_2$ complex; all other compounds precipitated out of this solution. Solubilization of the precipitates can be achieved by the addition of more acetone to the solvent system. This solubility mismatch precludes a thorough comparative study of the bimetallic interlocked species with their parent $\mathbf{1a/b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$ pseudorotaxanes (an acetone – water ratio higher than 5: 0.6 led to the precipitation of the anionic axles); as such, only the $\mathbf{2b}\cdot[\text{SnMe}_3]_2 \subset \mathbf{3}$ pseudorotaxane is included in Table 1.

The ^1H -NMR spectra recorded after the addition of the metallic salts to the “rota-ligands” are similar with the spectra of the $\mathbf{1a/b}\cdot[\text{NH}_4]_2 \subset \mathbf{3}$ pseudorotaxanes described above: three different sets of peaks can be observed, corresponding to the free $\mathbf{2a/b}\cdot[\text{M}]_2$ complexes, the unthreaded crown ether, and the bimetallic $\mathbf{2a/b}\cdot[\text{M}]_2 \subset \mathbf{3}$ interlocked species. While the signals associated with the organic groups attached to the metallic center (Me_3Sn , Ph_3Sn , $(\text{PPh}_3)_2\text{Cu}$) are observed, it is not possible to differentiate between the groups belonging to the unthreaded bimetallic complexes and those appended to the bimetallic interlocked species, presumably because they are too far from the **NDI** $\subset$ **15DN38C10** region.

These results show that the anionic **1a/b**-[NH₄]₂ **3** pseudorotaxanes are sufficiently robust to withstand the ensuing coordination process to metallic centers, with the formation of neutral bimetallic (pseudo)rotaxanes.

Table 1. Association constants (K_a)^a and free energies of complexation (ΔG°)^b for pseudorotaxanes **1**-[NH₄]₂ **3** and **2**-[M]₂ **3** at 25°C.

Solvent	Pseudorotaxane	K_a (M ⁻¹)	ΔG° (kJmol ⁻¹)
Acetone-d ₆ : D ₂ O 5.0/0.6 (v/v)	1a -[NH ₄] ₂ 3	896.5	- 16.9
	1a -[NH ₄] ₂ 3 ^c	758.7	- 16.4
	1b -[NH ₄] ₂ 3	1259.1	- 17.7
	1b -[NH ₄] ₂ 3 ^c	1131.5	- 17.4
	2b -[SnMe ₃] ₂ 3	562.7	- 15.7
CDCl ₃	2a -[SnMe ₃] ₂ 3	88.3	- 11.1
	2b -[SnMe ₃] ₂ 3	787.8	- 16.5
	2a -[SnPh ₃] ₂ 3	66.1	- 10.4
	2b -[SnPh ₃] ₂ 3	95.9	- 11.3
	2a -[Cu(PPh ₃) ₂] ₂ 3 ^d	-	-
	2b -[Cu(PPh ₃) ₂] ₂ 3 ^d	-	-

^a Determined by the single-point method using initial concentrations of axle and wheel of $1.66 \cdot 10^{-3}$ M and the integral values of the H_a resonances for threaded and unthreaded axles; errors are estimated to be 10% or less; ^b calculated using the formula $\Delta G^\circ = -RT \ln K_a$; ^c measured in the presence of excess of NH₄PF₆; ^d no pseudorotaxane peaks were observed.

Pseudorotaxane formation starting from the neutral, bimetallic axles (path II) was studied in CDCl₃. Upon mixing equimolar amounts of axles and wheel and recording their NMR spectra, pseudorotaxane formation was observed in only a few cases, Fig. 3. As a general trend, the coordination of the -PS₂ donor set to the metallic centers leads to very low K_a values or no pseudorotaxane formation at all (Fig. 3, Table 1), **2b**-[SnMe₃]₂ **3** being the only exception to the rule.

The results from investigating paths I and II toward pseudorotaxane formation, combined with the structural characteristics of the unthreaded bimetallic compounds [12], show that there are two factors influencing the interaction between the axles and the wheel: the *size* of the stopper and the *length* of the side-arms of the axles. While for both anionic axles **1a**-[NH₄]₂ and **1b**-[NH₄]₂ the size of the (An)PS₂ group alone is not bulky enough to prevent threading, in the case of **1a**-[NH₄]₂ the shorter side-arms of the axle place the dithiophosphonate groups in close proximity to the **NDI** core, thus protecting it from the crown ether **3**, which has as a consequence a lower K_a value for **1a**-[NH₄]₂ **3** compared to that for **1b**-[NH₄]₂ **3** (896 M⁻¹ vs. 1259 M⁻¹).

It is clear that in the case of **2a/b**-[Cu(PPh₃)₂]₂ axles the stoppers are bulky enough to prevent the slippage of crown **3** regardless of the length of the side-arms. This implies that using (PPh₃)₂CuNO₃ as the metal source in path I, the formation of a rotaxane can be expected. In the case of **2a/b**-[SnPh₃]₂ axles, the size of the (An)PS₂SnPh₃ groups permits to a very small extent the threading process. However, the length of their side-arms has little influence over the K_a values (66 M⁻¹ vs. 95 M⁻¹), suggesting that in this

case the size of the stopper is the limiting factor in pseudorotaxane formation. In the case of **2a/b**-[SnMe₃]₂ axles, the smaller size of the (An)PS₂SnMe₃ stopper makes threading possible, as indicated by the K_a value of 787 M⁻¹ for the **2b**-[SnMe₃]₂ ⋮ **3** pseudorotaxane. However, **2a**-[SnMe₃]₂ ⋮ **3** shows a very small K_a value (88 M⁻¹), explained by the shorter side-arms of the axle which would place the (An)PS₂SnMe₃ stoppers in the vicinity of the NDI core, thus hampering the rotaxation process. Comparing the association constants for the **1b**-[NH₄]₂ ⋮ **3** / **2b**-[SnMe₃]₂ ⋮ **3** pair in the acetone-water solvent system (**2b**-[SnMe₃]₂ is the only compound soluble in this solvent system), it can be observed that the coordination of the -PS₂ group to the Me₃Sn(IV) center (and consequently the increase in the bulkiness of the axle termini) significantly lowers the K_a value (1259 M⁻¹ vs. 562 M⁻¹, see Table 1).

Fig. 3. ¹H-NMR spectra of equimolar mixtures of bimetallic axles and crown **3** in CDCl₃.

2.3. Solid state studies

As mentioned above, addition of the metallic salts to the acetone-water solutions of the anionic pseudorotaxanes resulted in the formation of mixtures of unthreaded bimetallic axles and bimetallic pseudorotaxanes. In the case of **2b**-[SnPh₃]₂ ⋮ **3**, vapor diffusion of Et₂O into the aqueous acetone solution of the components produced deep red single crystals, which were used in X-ray diffraction experiments. There are two independent interlocked molecules in the unit cell, both having the -PS₂ groups coordinated in a monodentate fashion to the tin atom. A notable difference between the two independent molecules is that in one the Sn center is tetra-coordinate (Fig. 4a), while in the other, a water molecule expands the tin coordination number to five (Fig. 4b). There are two angular parameters (τ_4 and τ_5) used to describe the geometry around four and five-coordinated metallic centers [15]. The formula for calculating the τ_4 parameter is based on the sum of the two largest angles subtracted from 360, then all divided by 141 [15a]. The obtained values would range from 1.00 for a perfect tetrahedral geometry to 0.00 for a perfect square planar geometry. The τ_5 parameter is calculated by dividing the difference between the two largest angles by 60; a trigonal bipyramidal structure would produce a value of 1.00, while a square pyramidal structure would produce a value of 0.00 [15b]. Applying these formulae to our

case, the tin atoms are very close to a perfect tetrahedral ($\tau_4 = 0.95$) and trigonal bipyramidal ($\tau_5 = 0.91$) geometries, respectively.

Comparing the coordination of the PS₂ donor group to the Sn(IV) centers, only small differences between their bond lengths and angles can be observed. The tetrahedral tin shows a shorter Sn – S covalent bond at Sn1B – S1B = 2.443 Å, while the corresponding value in the case of the penta-coordinated tin is Sn1A – S1A = 2.563 Å. The second sulfur atoms of the PS₂ group are involved in secondary bonds [16]: the tin – sulfur distances (Sn1B – S2B = 3.560 Å and Sn1A – S2A = 3.745 Å) are longer than the sum of their covalent radii (2.48 Å), but shorter than the sum of their van der Waals radii (3.97 Å), suggesting weak interactions between the sulphur and tin atoms.

The common structural feature of the independent molecules of the pseudorotaxane **2b**-[SnPh₃]₂ **3** (Fig. 4) consists of a **15DN38C10** wheel threaded by the **2b**-[SnPh₃]₂ axle, with the π -rich aromatic regions of the wheel stacked around the π -deficient **NDI** core. In the case of the tetra-coordinate tin pseudorotaxane, the perpendicular distance between the **NDI** and **15DN38C10** rings is 3.50 Å, while for the penta-coordinate tin pseudorotaxane the corresponding value is 3.48 Å.

Examining the crystal packing of **2b**-[SnPh₃]₂ **3**, no supramolecular interactions can be identified for the pseudorotaxane containing the tetra-coordinated tin atom. In contrast, looking at the penta-coordinated tin center, it can be observed that the hydrogen atoms from the water molecule bonded to the tin atom are involved in two hydrogen bonds with two oxygen atoms within a crown ether wheel from a neighboring pseudorotaxane molecule, see Fig. 5. The O...H distances are 1.91 Å and 1.73 Å, with the O – H – O angles of 173.8° and 170.1° respectively. This interaction contributes to different orientation of the side-arms of the two independent pseudorotaxanes. In the case of the tetra-coordinated tin atom, the side-arms are oriented toward the **NDI**-wheel recognition motif, while in the other case, the SnPh₃ and anisole moieties are oriented away from **15DN38C10** (see Fig. 4 for a space filling representation of the two molecules, emphasizing the two different orientations).

Another difference between the two molecules (presumably another consequence of the hydrogen bonding interaction described above) is the orientation of the central **NDI** core relative to the aromatic region of the crown ether, Fig. 6. This orientation can be measured by the torsion angle defined by the N_{NDI} – Ct_{NDI} – Ct_{15DN38C10} – C_{15DN38C10} angle.^{6a} In the case of the tetracoordinate tin pseudorotaxane, the torsion angle is 86.8° and for the pentacoordinate tin pseudorotaxane is 78°.

Fig. 4. Molecular structures of the two independent molecules of $2b\text{-[SnPh}_3\text{]}_2 \cdot 3$: a) the four-coordinate and b) the five-coordinate tin atom; selected bond lengths (Å) and angles (°): Sn1A – S1A = 2.5626(14); Sn1A – O11A = 2.457(4); Sn1A – C19A = 2.132(5); Sn1A – C25A = 2.140(5); Sn1A – C31A = 2.136(5); S1A – P1A = 2.0462(19); S2A – P1A = 1.934(2); Sn1B – C31B = 2.128(5); Sn1B – S1B = 2.4427(14); Sn1B – C19B = 2.135(6); Sn1B – C25B = 2.116(5); S1B – P1B = 2.0758(19); S2B – P1B = 1.9387(19); S1A – Sn1A – C19A = 101.35(14); S1A – Sn1A – C25A = 90.58(13); S1A – Sn1A – C31A = 99.05(15); S1A – Sn1A – O11A = 175.54(9); S1A – P1A – S2A = 117.18(10); S1B – Sn1B – C31B = 111.35(14); S1B – Sn1B – C19B = 100.82(15); S1B – Sn1B – C25B = 109.68(15); S1B – P1B – S2B = 115.00(8); c) and d) space filling representation of the two independent molecules; color code: C – green/yellow, H – black/grey, O – red, N – blue, S – yellow, P – orange, Sn – purple.

Fig. 5. Hydrogen bonding involving the coordinated water molecule and the crown ether: a) two pseudorotaxanes held together by hydrogen bonding; b) detail of the hydrogen bonds; c) space filling of the atoms involved in hydrogen bonding.

Fig. 6. The different relative orientation between the **NDI** core relative and the aromatic region of the crown ether: a) the tetra-coordinate tin pseudorotaxane; b) the penta-coordinate tin pseudorotaxane.

3. Conclusions

We reported here the synthesis and characterization of two negatively charged axles with a **NDI** core, capable of interacting with the **15DN38C10** crown ether to form anionic pseudorotaxanes. These interlocked species interact with Sn(IV) and Cu(I) metallic centers, with the formation of neutral (counter-ion free) bimetallic (pseudo)rotaxanes. To the best of our knowledge, these are the first examples of anionic pseudorotaxanes with donor properties that generate, upon coordination to cationic metal centers, such interlocked neutral species.

The successful synthesis of these species shows the potential of this method for the future preparation of more complex metal-based interlocked architectures. For example, the use of metallic systems with an overall charge of 2+ should yield at least mono-dimensional rotaxane-based coordination polymers through the coordination of two -PS₂ groups from two different pseudorotaxanes to the same metal (the side-arms of the axles are not long enough to allow the formation of the corresponding monometallic catenanes).

Importantly, the **NDI** group can be easily functionalized with other negatively charged side-arms, containing the carboxylate and/or dithiocarbamate donor groups, thus opening the door for the synthesis of a large variety of neutral, interlocked arrays, either discrete species self-assembled *via* secondary bonds or “classic,” coordinatively bonded coordination polymers.

4. Experimental

4.1. General considerations

Unless otherwise noted, all operations were carried out in open air. Operations requiring inert (nitrogen) atmosphere were carried out using standard Schlenk techniques and an MBraun LabStar dry-box. When needed, solvents were dried by conventional methods and distilled under a dry N₂ atmosphere

immediately prior to use. Elemental analyses were performed by Robertson Microlit Laboratories, NJ. NMR spectra were recorded by using a 400 MHz Bruker Avance FT-NMR Spectrometer and a Varian Mercury/VX 400 Spectrometer. Electrospray ionization mass spectrometry data were obtained on a MicroMass QTOF spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. The axles **1a**-[NH₄]₂, **1b**-[NH₄]₂, **2a**-[SnPh₃]₂, **2a**-[Cu(PPh₃)₂]₂, **2b**-[SnPh₃]₂, and **2b**-[Cu(PPh₃)₂]₂ [12], and the **15DN38C10** crown ether [17] were prepared according to published procedures. All other reagents are commercially available (Sigma-Aldrich) and were used without further purification.

4.2. Synthesis of NDI-[CH₂CH₂O(An)PS₂(SnMe₃)₂]₂ (**2a**-[SnMe₃]₂)

A 250 mL flask was charged with a stirring bar and a solution of Me₃SnCl (0.0498 g, 0.25 mmol) in DCM (75 mL). To this colorless solution was added, under vigorous stirring, an orange aqueous solution of **1a** (0.0991 g, 0.125 mmol) in 75 mL water, and the mixture was stirred for an additional 12 hours. The completion of the reaction was indicated by the loss of the color of the aqueous phase and the appearance of an orange color in the organic phase. The organic phase was separated, and the aqueous phase extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and removed under reduced pressure, to afford the desired compound as an orange solid (0.0722 g, 53.3 %). ¹H-NMR (400 MHz, CDCl₃): δ = 8.73 (s, 4H, NDI), 7.80 (m, 4H, MeO-C₆H₄-P), 6.82 (m, 4H, MeO-C₆H₄-P), 4.61 (m, 4H, -CH₂-), 4.46 (m, 4H, -CH₂-), 3.79 (s, 6H, -O-CH₃), 0.53 (s, J_{H-Sn} = 27.8 Hz, 18H, Sn(CH₃)₃). Anal. Calcd. for C₃₈H₄₄N₂O₈P₂S₄Sn₂: C = 42.09, H = 4.09, N = 2.58; Found: C = 42.21, H = 3.89, N = 2.77.

4.3. Synthesis of NDI-[CH₂CH₂OCH₂CH₂O(An)PS₂(SnMe₃)₂]₂ (**2b**-[SnMe₃]₂)

A 250 mL flask was charged with a stirring bar and a solution of Me₃SnCl (0.0498 g, 0.25 mmol) in DCM (75 mL). To this colorless solution was added, under vigorous stirring, an orange aqueous solution of **1b** (0.110 g, 0.125 mmol) in 75 mL water, and the mixture was stirred for an additional 12 hours. The completion of the reaction was indicated by the loss of the color of the aqueous phase and the appearance of an orange color in the organic phase. The organic phase was separated, and the aqueous phase extracted with DCM (3 x 10 mL). The combined organic phases were dried over anhydrous Na₂SO₄ and removed under reduced pressure, to afford the desired compound as an orange solid (0.0952 g, 64.9 %). ¹H-NMR (400 MHz, CDCl₃): δ = 8.69 (s, 4H, NDI), 7.81 (m, 4H, MeO-C₆H₄-P), 6.84 (m, 4H, MeO-C₆H₄-P), 4.47 (m, 4H, -CH₂-), 4.14 (m, 4H, -CH₂-), 3.88 – 3.83 (m, 10H, 4H -CH₂- overlap with 6H -O-CH₃), 3.77 (m, 4H, -CH₂-), 0.59 (s, J_{H-Sn} = 28.2 Hz, 18H, Sn(CH₃)₃). Anal. Calcd. for C₄₂H₅₂N₂O₁₀P₂S₄Sn₂: C = 43.02, H = 4.47, N = 2.39; Found: C = 43.39, H = 4.38, N = 2.62.

4.4. General procedure for pseudorotaxane synthesis and crystal growing procedure

As indicated by the VT-NMR experiments, the association constant of the pseudorotaxanes is significantly increased at 0° C. Therefore, acetone-water solutions of the axle and crown (0.1 mmol each) were stirred for 2 hours in an ice-water bath. To the red solutions, solid R₃SnCl (R = Me, Ph) or (Ph₃P)₂CuNO₃ was added, and the stirring was continued overnight. To the resulting suspensions enough acetone was added dropwise (ca. 1 mL) to dissolve the precipitates. The resulting red solutions were each

divided in about 0.5 mL portions and transferred in vials which were subsequently placed in larger vials already filled with about 15 mL of diethyl ether. The large vials were tightly closed and kept at 0° C for several days, during which time, in the case of **2b**-[SnPh₃]₂ **3**, red crystals formed and used for single crystal X-ray diffraction analysis.

4.5. Crystallographic studies

Crystallographic details for compounds **2b**-[SnPh₃]₂ **3** are summarized in Table 2. The X-ray data were collected at 100 K on a Bruker SMART APEXII CCD diffractometer equipped with Cu K α radiation. Intensities were collected using phi and omega scans and were corrected for Lorentz polarization and absorption effects. The *X-SEED* software platform [18], equipped with *SHELXS* and *SHELXL* modules on a PC computer [19], was used for all structure solution and refinement calculations and molecular graphics. The structure was solved by direct methods, and refined by anisotropic full-matrix least-squares for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined using a riding model with fixed thermal parameters.

Table 2. Crystal data and details for **2b**-[SnPh₃]₂ **3**.

	2b -[SnPh ₃] ₂ 3
Empirical Formula	C ₂₁₆ H ₂₂₀ N ₄ O ₄₂ P ₄ S ₈ Sn ₄
FW, g · mol ⁻¹	4399.24
Crystal System	Triclinic
Space Group	<i>P</i> 1
T (K)	100(2)
<i>a</i> , (Å)	11.6038(4)
<i>b</i> , (Å)	16.3167(6)
<i>c</i> , (Å)	27.3486(9)
α , (°)	88.799(2)
β , (°)	78.172(2)
γ , (°)	83.306(2)
<i>V</i> , (Å ³)	5033.6(3)
<i>Z</i> , <i>Z'</i>	1
<i>D_x</i> (mg·m ⁻³)	1.451
<i>F</i> (000)	2268
<i>R/R_w</i> ² (obs data)	0.054/0.138
<i>S</i>	1.05
no. of reflns / params	17677/1330
$\Delta\rho_{\text{max/min}}$ (e·Å ⁻³)	+ 0.98/ − 0.61

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Graphical Abstract

Neutral (pseudo)rotaxanes have been prepared from anionic axles threaded through the cavity of the bis-1,5-(dinaphtho)-38-crown-10 ether and subsequent coordination to cationic Sn(IV) and Cu(I) metallic centers.