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Complexes of a [2]rotaxane ligand with terminal terpyridine groups†

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Permanently interlocked [2]rotaxane ligands can be created by capping a pyridine terminated [2]pseudorotaxane with terpyridine containing stoppers. The robust nature of the resulting [2]rotaxane ligand allows coordination to inert metals such as Ru(II) not possible under standard self-assembly conditions.

Combining the physical properties of transition metals (electronic, magnetic and catalytic) with the dynamic properties of mechanically interlocked molecules (MIMs) has the potential to create chemical systems with a variety of unique applications, the scope of which, are just beginning to be explored.¹ For example, a number of MIM systems have been reported in which a transition metal acts as 1) a templating ion to facilitate interpenetration,² 2) a reporter group to sense binding of a guest,³ 3) an additive that elicits molecular motion⁴ or 4) a building block to create metal organic frameworks (coordination polymers).⁵ However, the synthesis of such sophisticated ligands and their transition metal complexes still present a major challenge for synthetic inorganic chemists.

Probably, the most common and facile method of preparing an interlocked coordination compound is by self-assembly. In such cases, the axle, the wheel and a labile metal fragment are mixed under mild conditions leading to both threading of the axle through the wheel and stoppering of the axle via metal coordination to create an interlocked [2]rotaxane. We originally⁶ stoppered the [2]pseudorotaxane [1 DB24C8]²⁺ with the Pd(II) pincer complex $[Pd(C_6H_3(CH_2SPh)_2)]^+$ and later reported this could easily be accomplished using simple anionic fragments such [MnBr₃]⁻ and [CoBr₃]⁻ yielding neutral, zwitterionic complexes.⁷ Since the preparation of these metal stoppered rotaxanes required employing experimental conditions that favoured both [2]pseudorotaxane formation and metal ligand coordination, the types of complexes that could be prepared were restricted to those readily formed at room temperature in non-competitive solvents. These self-assembly conditions produced good yields of complexes with labile transition metal ions⁸ but were not sufficient for preparing robust complexes of inert transition metal ions that required much more forcing conditions and/or were not reversible under the milder conditions used.

A practical method of incorporating inert metal ions directly into an interlocked species would be to construct a ligand that was itself a permanently interlocked rotaxane.⁹ This would allow for the adoption of forcing conditions such as elevated temperature and highly polar solvents since unthreading of the rotaxane unit would not be possible. As an example of this approach, we have prepared a bis(terpy) (terpy = 2,2',6',2''-terpyridine) rotaxane ligand by stoppering the [2]pseudorotaxane¹⁰ [1 \subset DB24C8]²⁺ with 4'-(4-tolyl)-2,2',6',2''-terpyridine groups to produce the rotaxane ligand [2 \subset DB24C8]⁴⁺ as outlined in Scheme 1. 4'-(4-Bromobenzyl)-2,2',6',2''-terpyridine¹¹ was prepared in 35% yield by bromination of 4'-(4-tolyl)-2,2',6',2''-terpyridine¹¹ using



Scheme 1 Preparation of the [2]rotaxane ligand: *i*) 3 equiv. of 4'-(4-bromobenzyl)-2,2',6',2''-terpyridine, MeNO₂, room temperature, 7 days followed by anion exchange by stirring the MeNO₂ layered with NaOTf(aq) for 10 h; isolated yield 31%.

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N-bromosuccinamde in CCl₄ solution and two equivalents of the resulting benzylbromide derivative used to alkylate the terminal pyridine groups of the [2]pseudorotaxane $[1 \subset DB24C8]^{2+}$ producing [2]rotaxane $[2 \subset DB24C8]^{4+}$ in 31% yield.

In order to explore the coordination of both labile and inert metal ions to $[2 \subset DB24C8]^{4+}$, complexes of Zn(II) and Ru(II) were prepared. For Zn(II), $[2 \subset DB24C8][OTf]_4$ was stirred with $[Zn(H_2O)_6][OTf]_2$ in MeCN solution for 12 h at room temperature yielding an orange solution. The ¹H NMR spectrum of the resulting complex showed only broadened resonances for $[2 \subset DB24C8]^{4+}$ due to rapid metal ligand exchange.

Diffusion of *iso*-propyl ether into a MeNO₂ solution of the complex produced essentially quantitative yield of an orange crystalline material. A single crystal X-ray diffraction study[‡] showed this material to be binuclear with a Zn(II) ion coordinated to each terpyridine group. Fig. 1 shows a ball-and-stick representation of one of the $[(Zn(H_2O)_3)_2(2 \subset DB24C8)]^{8+}$ cations. The dumbbell



Fig. 1 A ball-and-stick representation of the cationic portion of the X-ray crystal structure of $[(Zn(H_2O)_3)_2(2 \subset DB24C8)]^{8+}$. The complex occupies a crystallographic centre of symmetry. All hydrogen atoms, except those on coordinated water molecules, all anions and all solvent molecules have been omitted for clarity. (Zn = blue-gray, O = red, N = blue, C = black, H = white; wheel bonds = silver, axle bonds = gold).

component adopts a zig-zag shaped conformation that is linear through the central interlocked component but bent at the benzylic methylene units that link the terpyridine groups to the rest of the molecule. The **DB24C8** wheel is in the S-shaped conformation most commonly observed for this templating motif.¹⁰ The complex is over 4 nm in length with a $Zn(II) \cdots Zn(II)$ distance of 37.1 Å.

For Ru(II), [2⊂DB24C8][OTf]₄ was refluxed with [RuCl₃(terpy)]¹² in a 1:1 EtOH/H₂O solution for 24 h yielding a deep red solution. These are the standard conditions for the preparation of heteroleptic terpyridine complexes such as [Ru(terpy)(terpy')]²⁺.¹² The ¹H NMR spectrum of the resulting complex (Fig. 2) clearly shows formation of the binuclear product [(Ru(terpy))₂(2⊂DB24C8)]⁸⁺; NMR assignments were confirmed by 2D COSY and NOESY spectra. The axle 2^{2+} exhibits significant chemical shift changes due to both interpenetration through the DB24C8 wheel as well as coordination to Ru(II). The interpenetration effects methylene protons a and aromatic protons b which are involved in hydrogen bonding to oxygen atoms of the crown ether resulting in $\Delta\delta$ of 0.33 and 0.30 ppm respectively¹⁰ while π -stacking between the electron rich aromatic rings of **DB24C8** and the electron poor pyridinium groups on the axle results in significant shielding and $\Delta\delta$ of -0.21 and -0.18 ppm for protons c and d respectively.¹⁰ Rotation of the pyridine groups of (2 CDB24C8)²⁺ into favourable conformations for coordination and bonding to the Ru(II) centre results in coordination shifts for *i*-*m* ranging from a $\Delta\delta$ of -1.31 ppm for *m* to +0.26 ppm for *i*.



Fig. 2 The ¹H NMR spectrum of the binuclear [2]rotaxane complex $[(Ru(terpy))_2(2 \Box DB24C8)][OTf]_8$ in MeCN-d₃ solution at 298 K. The labelling scheme is shown in Scheme 1.

The UV-visible absorption spectrum of $[(Ru(terpy))_2-(2 \subset DB24C8)]^{8+}$ in MeCN solution showed a single MLCT absorption peak at $\lambda_{max} = 485$ nm. This is comparable to $\lambda_{max} = 483$ nm observed for $[Ru(terpy)(4'-(4-tolyl)terpy)]^{2+}$.¹³ The red shifts from $\lambda_{max} = 474$ nm observed for $[Ru(terpy)_2]^{2+}$ can be attributed to the presence of the electron donating tolyl group.¹⁴

Diffusion of *iso*-propyl ether into a MeNO₂ solution of $[(Ru(terpy))_2(2 \subset DB24C8)][OTf]_8$ yielded X-ray quality crystals.[‡] Fig. 3 shows a ball-and-stick-representation of the complex cation, $[(Ru(terpy))_2(2 \subset DB24C8)]^{8+}$. As was observed for the Zn(II) complex, the dumbbell adopts a zig-zag shaped conformation that is essentially linear throughout the interlocked component but bent at the benzylic methylene units linking the terpyridine and





Fig. 3 A ball-and-stick representation of the cationic portion of the X-ray crystal structure of $[(Ru(terpy))_2(2 \subset DB24C8)]^{8+}$. The complex occupies a crystallographic centre of symmetry. All hydrogen atoms and anions have been omitted for clarity. (Ru = blue-gray, O = red, N = blue, C = black, H = white; wheel bonds = silver, axle bonds = gold).

pyridinium groups. The two different terpyridine groups chelate to Ru(II) in a perpendicular fashion with bond distances and angles typical for Ru(II) bis(terpyridine) complexes. Again, the total length of the complex is over 4 nm with a $Ru(II) \cdots Ru(II)$ distance of 36.5 Å.

Conclusions

Preparation of a binuclear Zn(II) complex of $[2 \subset DB24C8]^{4+}$ with labile co-ligands (H₂O) shows that this ligand has the potential

to be used in self-assembly reactions to create 1-periodic terpylinked coordination polymers. More importantly, the synthesis of a mixed ligand complex of an inert metal ion, such as Ru(II), clearly demonstrates that the "rotaxane as a ligand" approach provides a methodology to prepare robust complexes that require harsh reaction conditions and/or to facilitate stepwise coordination of different ancillary ligands; in this case terpy followed by rotaxane.

Notes and references

data15 ‡ Crystal for $[(Zn(H_2O)_3)_2(2 \subset DB24C8)][(Zn(H_2O)(BF_4))_2$ $(2 \subset DB24C8)$][OTf]₇(MeNO₂)₃: C₂₀₀H₂₁₀B₂F₅₀N₂₆O₈₂S₁₄Zn₄, M = 5971.88, T = 173(2)K, monoclinic, space group $P2_1/c$, a = 24.665(14), b = 173(2)K, monoclinic, space group $P2_1/c$, a = 24.665(14), b = 10026.270(15), c = 21.104(12) Å, $\beta = 108.612(7)$, V = 12959(13) Å³, $\rho_{\rm c} = 1.530$ g cm⁻³, $\mu = 0.603$ mm⁻¹, Z = 2, reflections collected = 121682 ($R_{int} = 0.7726$), final R indices [$I > 2\sigma I$]: $R_1 = 0.1241$, w $R_2 =$ 0.2584, R indices (all data): $R_1 = 0.4350$, $wR_2 = 0.4726$, GoF = 0.934 with data/variables/restraints = 22775/1531/476. Crystal data for $[(Ru(terpy))_2(2 \subset DB24C8)][OTf]_6[Cl]_2.(MeNO_2)_4: C_{130}H_{118}Cl_2F_{18}N_{20}O_{34}$ Ru₂S₆, M = 3311.84, T = 173(2)K, triclinic, space group $P\overline{1}$, a = 14.056(3), b = 14.073(3), c = 22.616(5) Å, $\alpha = 78.454(4), \beta = 83.369(4), \gamma = 62.894(3), \gamma = 62.894(3), \beta = 83.369(4), \gamma = 83.369(4),$ V = 3900.2(16) Å³, $\rho_c = 1.401$ g cm⁻³, $\mu = 0.406$ mm⁻¹, Z = 1, reflections collected = 37004 ($R_{int} = 0.1452$). Before SQUEEZE:¹⁶ R indices [I > $2\sigma I$]: $R_1 = 0.1627$, $wR_2 = 0.3859$, R indices (all data): $R_1 = 0.3037$. $wR_2 = 0.3037$ 0.4588, GoF = 1.297 with data/variables/restraints = 11259/928/355. After SQUEEZE: *R* indices $[I > 2\sigma I]$: $R_1 = 0.1212$, $wR_2 = 0.2830$, *R* indices (all data): $R_1 = 0.2567$. $wR_2 = 0.3350$, GoF = 0.890 with data/variables/restraints = 13674/928/502.

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