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Zwitterionic [2]rotaxanes utilising anionic transition metal stoppers

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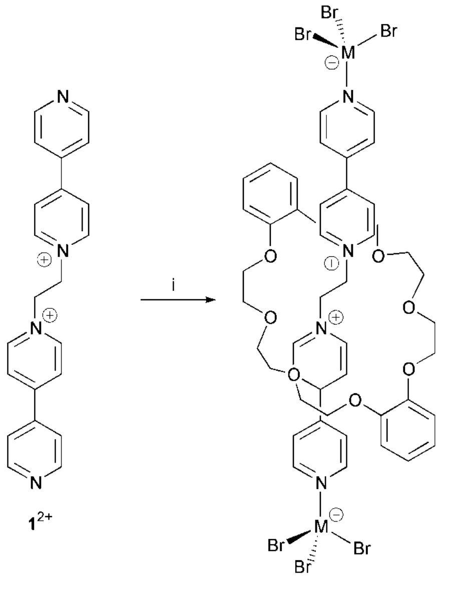
Zwitterionic [2]rotaxanes are formed when anionic $[MBr_3]^-$ (M = Co(II), Mn(II)) units are used as stoppers for 1,2-bis(pyridinium)ethane/dibenzo-24-crown type axles.

The formation of rotaxanes, including molecular shuttles and other so-called molecular machinery, involves the incorporation of bulky stopper groups to prevent unthreading of the axle component from the wheel unit.[1] The "threading-followed-by-stoppering" method has given rise to a number of strategies to incorporate stoppers. Some more popular examples include alkylation of amines[2] and phosphines,[3] ester, carbonate and acetal formation,[4] oxidative coupling,[5] cycloaddition,[6] Wittig reactions,[7] and coordination chemistry.[8] Often the final dumbbell shaped axle contains multiple positive charges and the stoppering groups can contribute to this charge build-up; the incorporation of metal ions being a major culprit. If these mechanically linked species are to be assembled on surfaces or incorporated into solid state devices it would be advantageous for them to be rendered neutral, *i.e.* not to be accompanied by counter ions.[9] Although there are some neutral, zwitterionic systems known,[10] these are rare and we were interested in finding a convenient method for negating the positive charges of the axle upon stoppering. We report herein the use of very simple anionic metal $[MBr_3]^-$ (M = Co(II), Mn(II)) fragments as stoppers to meet this objective.

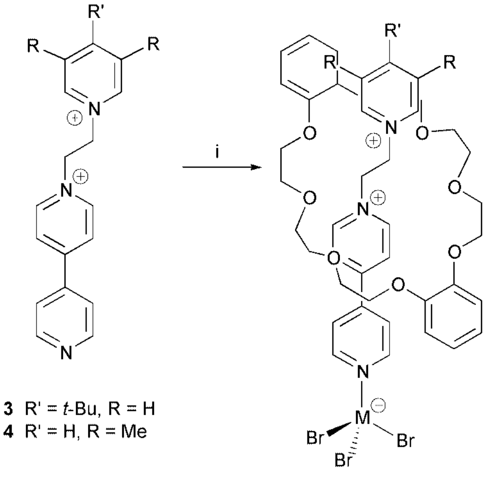
Mixing 1,2-bis(4,4′-dipyridinium)ethane, $\mathbf{1}^{2+}$, as the bromide salt, with two equivalents of dibenzo-24-crown-8 (DB24C8) in $MeNO_2$, instantaneously forms the [2]pseudorotaxane $(\mathbf{1}/\text{DB24C8})^{2+}$.[11] † Addition of two equivalents of anhydrous MBr_2 (M = Co(II), Mn(II)) in $MeNO_2$ immediately produces the neutral zwitterionic [2]rotaxane complexes **2a** (Co) and **2b** (Mn) as emerald green and yellow solids respectively (Scheme 1). X-Ray diffraction studies on both compounds ‡ showed that the combination of a bromide counter ion from the pyridinium axle and two bromide ligands from each metal resulted in the formation of anionic MBr_3^- stoppers, which coordinate in a tetrahedral geometry to the terminal pyridine units. Although these are simple complexes, surprisingly few examples of this type of zwitterion are known.[12]



1^{2+}

2a M = Co(II)
2b M = Mn(II)

Scheme 1 Reagents and conditions: i, Two equivalents DB24C8 and two equivalents MBr_2 in $MeNO_2$ at room temperature.



3 R′ = *t*-Bu, R = H
4 R′ = H, R = Me

5a R′ = *t*-Bu, R = H, M = Co(II)
6a R′ = H, R = Me, M = Co(II)
5b R′ = *t*-Bu, R = H, M = Mn(II)
6b R′ = H, R = Me, M = Mn(II)

Scheme 2 Reagents and conditions: i, Two equivalents DB24C8 and one equivalent MBr_2 in $MeNO_2$ at room temperature.

Fig. 1 shows the crystal structure of the neutral di-zwitterion **2a** (Co); **2b** (Mn) is isomorphous. Although very simple, the pyramidal MBr_3 unit acts as the inorganic equivalent of a *t*-Bu group and easily prevents unthreading of the DB24C8 wheel. The non-covalent interactions (hydrogen bonding and π-stacking) between the 1,2-bis(4,4′-dipyridinium)ethane group and the DB24C8 unit are unperturbed in the presence of these anionic stoppers. C–H···O interactions shown in Fig. 1 are typical for this type of rotaxane and range from 2.31–2.59 Å.

In order to demonstrate the general utility of these anionic stoppers, the new asymmetric axles $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ were prepared and converted to [2]rotaxanes **5a** (Co), **5b** (Mn) and **6a** (Co), **6b** (Mn) respectively by adding two equivalents of DB24C8 and capping with one equivalent of $[MBr_3]^-$ (Scheme 2). § These complexes are soluble in polar non-coordinating solvents ($MeNO_2$) and can be prepared easily in a matter of seconds.

UV-Vis absorption spectroscopy verified that the zwitterionic structure observed in the solid state is preserved in solution. The visible spectrum of **5a** is shown in Fig. 2. Two distinct features with λ_{max} values of 685 and 388 nm dominate the spectrum. These are due respectively to the high energy band

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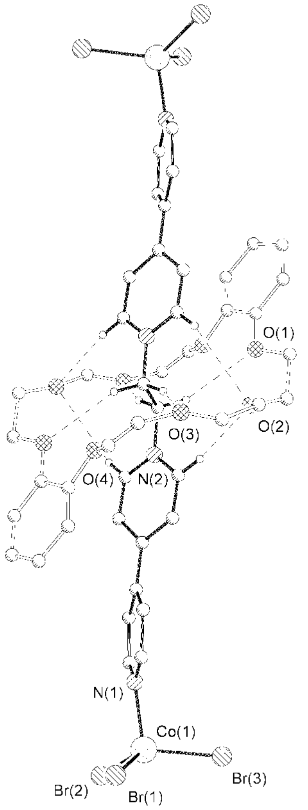

Fig. 1 Drawing of **2a** showing the basic numbering scheme. The molecule has crystallographic inversion symmetry. Selected distances (Å) and angles (°): Co–Br(1) 2.372(3), Co–Br(2) 2.394(3), Co–Br(3) 2.373(3), Co–N(1) 2.039(13), Br(1)–Co(1)–Br(2) 114.75(11), Br(1)–Co(1)–Br(3) 112.04(11), Br(2)–Co(1)–Br(3) 115.91(10), Br(1)–Co(1)–N(1) 105.8(4), Br(2)–Co(1)–N(1) 102.6(3), Br(3)–Co(1)–N(1) 104.1(4), Co(1) · · · Co(1) 21.6.

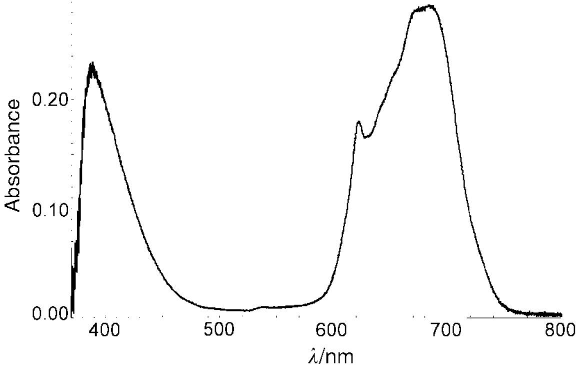

Fig. 2 UV-Vis absorption spectrum for **5a** ($MeNO_2$, 1.0×10^{-3} M).

($^4A_2 \longrightarrow {}^4T_1(P)$) of the tetrahedral [$CoBr_3N$] metal centre[13] and the CT band resulting from the interaction of π-electron rich DB24C8 and π-electron poor pyridinium aromatic rings in the [2]rotaxane. Interestingly the commonly observed colours for these separate components in analogous compounds are intense blue for tetrahedral Co(II) ions and yellow for the [2]pseudorotaxane [**3**/DB24C8]$^{2+}$ while **5a** is emerald green as a result of this combination. Analogous $MnBr_3$ capped [2]rotaxanes show the CT band but only a featureless baseline above 500 nm consistent with a tetrahedral spin forbidden d^5 ion.

MBr_3^- (Co, Mn) units are easily generated and attached as stoppers under conditions that favour rotaxane formation (room temperature and non-competitive solvents). These results suggest that this could be a general method amenable to a number of similar systems. The signature colour change associated with the Co(II) stoppers is particularly useful for identifying and isolating products.

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Notes and references

† [**1**]Br_2 was prepared by the literature procedure.[14]

‡ Crystal data for **2a**: $C_{46}H_{52}Br_6Co_2N_4O_8$, $M = 1379.75$, orthorhombic, space group *Pbca*, $a = 17.7244(2)$, $b = 14.7931(3)$, $c = 20.5958(3)$ Å, $U = 5400.2(2)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu = 4.586$ mm^{-1}, 3047 independent reflections ($R_{int} = 0.0999$). $R1 = 0.1028$, $wR2 = 0.1444$, ($I > 2\sigma(I)$), $R1 = 0.2805$, $wR2 = 0.3242$, (all data), goodness-of-fit (F^2) = 1.149.

Crystal data for **2b**: $C_{46}H_{52}Br_6Mn_2N_4O_8$, $M = 1378.23$, orthorhombic, space group *Pbca*, $a = 17.893(2)$, $b = 14.854(2)$, $c = 20.799(3)$ Å, $U = 5528.1(12)$ Å^3, $T = 293(2)$ K, $Z = 2$, $\mu = 4.844$ mm^{-1}, 3968 independent reflections ($R_{int} = 0.0355$). $R1 = 0.0407$, $wR2 = 0.0645$, ($I > 2\sigma(I)$), $R1 = 0.1058$, $wR2 = 0.1150$, (all data), goodness-of-fit (F^2) = 1.027. Data were collected on a Siemens SMART CCD instrument and solutions performed using the SHELXTL 5.03 Program Library (Siemens Analytical Instrument Division, Madison, WI, USA, 1997). CCDC reference numbers 168751 and 168752. See http://www.rsc.org/suppdata/dt/b1/b107257a/ for crystallograpic data in CIF or other electronic format.

§ Preparation of: [**3**]Br_2: a mixture of 1-bromo-2-(4,4′-dipyridinium)ethane bromide (1.0 g, 2.91 mmol) and 4-*tert*-butylpyridine (2.35 g, 17 mmol) in anhydrous EtOH (100 mL) was refluxed for 24 h. The solution was cooled to 0 °C and the precipitate collected and washed with Et_2O (3 × 25 mL). Yield: 0.45 g, 0.94 mmol (32%). [**4**]Br_2: a mixture of 1-bromo-2-(4,4′-dipyridinium)ethane bromide (3.0 g, 8.70 mmol) and 3,5-lutidine (5.61 g, 53 mmol) in anhydrous EtOH (100 mL) was refluxed for 72 h. The solution was cooled to 0 °C and the precipitate collected and washed with Et_2O (3 × 25 mL). Yield: 1.47 g, 3.23 mmol (37%).

Selected data for: [**3**]Br_2: ^{1}H NMR (D_2O, 300 K, 500 MHz): δ 8.93 (d, 2H, $J = 6.1$ Hz), 8.77 (d, 2H, $J = 4.7$ Hz), 8.69 (d, 2H, $J = 6.2$ Hz), 8.46 (d, 2H, $J = 6.0$ Hz), 8.12 (d, 2H, $J = 6.1$ Hz), 7.90 (d, 2H, $J = 4.9$ Hz), 5.33 (m, 2H), 5.29 (m, 2H), 1.38 (m, 9H). [**4**]Br_2: ^{1}H NMR (D_2O, 300 K, 500 MHz): δ 8.89 (d, 2H, $J = 6.3$ Hz), 8.82 (d, 2H, $J = 4.8$ Hz), 8.49 (s, 2H), 8.47 (d, 2H, $J = 6.3$ Hz), 8.32 (s, 1H), 7.91 (d, 2H, $J = 5.1$ Hz), 5.33 (m, 2H), 5.24 (m, 2H), 2.45 (m, 6H). **5a**: UV-Vis: (1.0×10^{-3} M, $MeNO_2$) 388 nm ($\varepsilon = 432$ L mol^{-1} cm^{-1}), 685 nm ($\varepsilon = 511$ L mol^{-1} cm^{-1}). **5b**: UV-Vis: (1.0×10^{-3} M, $MeNO_2$) 389 nm ($\varepsilon = 160$ L mol^{-1} cm^{-1}). **6a**: UV-Vis: (1.0×10^{-3} M, $MeNO_2$) 388 nm ($\varepsilon = 451$ L mol^{-1} cm^{-1}), 688 nm ($\varepsilon = 564$ L mol^{-1} cm^{-1}). **6b**: UV-Vis: (1.0×10^{-3} M, $MeNO_2$) 389 nm ($\varepsilon = 160$ L mol^{-1} cm^{-1}).

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