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Synthesis of a [2]Rotaxane Incorporating a Ni(II)–Salen Moiety: Evidence of Ring-Opening-and-Closing Protocol

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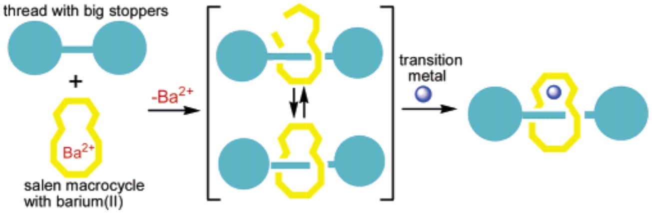
ABSTRACT



We have synthesized a [2]rotaxane from a crown-ether-like macrocycle that undergoes ring opening and closing through cleavage and formation of imino bonds of a salen moiety; the self-assembly of this macrocycle and a dumbbell-shaped rodlike component, followed by addition of nickel acetate, afforded, after counterion exchange, a [2]rotaxane that is stabilized through coordination of the Ni ion to the macrocycle's salen moiety.

Research into mechanically interlocked molecules has increased in recent years because of these molecules' many potential applications.[1] For example, Nolte's group[2] has reported a rare example of catalytically active rotaxanes. Because transition-metal complexes of salen [*N*,*N*′-ethylenebis(salicylideneiminato)dianion] and salophen [*N*,*N*′-*o*-phenylenebis(salicylideneiminato)dianion] compounds are particularly interesting catalysts,[3] we wished to incorporate them into rotaxane structures. The Stoddart group has described the synthesis of [2]rotaxanes based on the clipping of a macrocycle about a dialkylammonium ion-based dumbbell and subsequent reduction of imino bonds;[4] the mechanisms for the ring opening and closing of imine bonds have been described by the Wild group.[5] In this paper, we provide evidence for ring opening and closing in macrocycles through the cleaving and forming of the imino bonds of salen

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(1) (a) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 333−337. (b) Jun, S. I.; Lee, J. W.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Tetrahedron Lett.* **2000**, *41*, 471−475. (c) Feringa, B. L. *Molecular Switches*; VCH: Weinheim, 2001. (d) Schalley, C. A.; Beizai, K.; Vögtle, F. *Acc. Chem. Res.* **2001**, *34*, 465−476. (e) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477−487. (f) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174−179. (g) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845−1849. (h) Feng, M.; Guo, X.; Lin, X.; He, X.; Ji, W.; Du, S.; Zhang, D.; Zhu, D.; Gao, H. *J. Am. Chem. Soc.* **2005**, *127*, 15338−15339.

(2) Thordarson, P.; Bijsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. *Nature* **2003**, *424*, 915−918.

(3) (a) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189−214. (b) Wöltinger, J.; Bäckvall, J.-E.; Zsigmond, Á. *Chem.−Eur. J.* **1999**, *5*, 1460−1467. (c) Castelli, V. v. A.; Cort, A. D.; Mandolini, L.; Reinhoudt, D. N.; Schiaffino, L. *Eur. J. Org. Chem.* **2003**, 627−633. (d) Taylor, M. S.; Zalatan, D. N.; Lerchner, A. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2005**, *127*, 1313−1317. (e) Liu, S.-Y.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 5278−5279.

(4) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1870−1875.

(5) (a) Gugger, P. A.; Hockless, D. C. R.; Swiegers, G. F.; Wild, S. B. *Inorg. Chem.* **1994**, *33*, 5671−5677. (b) Hockless, D. C. R.; Lindoy, L. F.; Swiegers, G. F.; Wild, S. B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 117−122.

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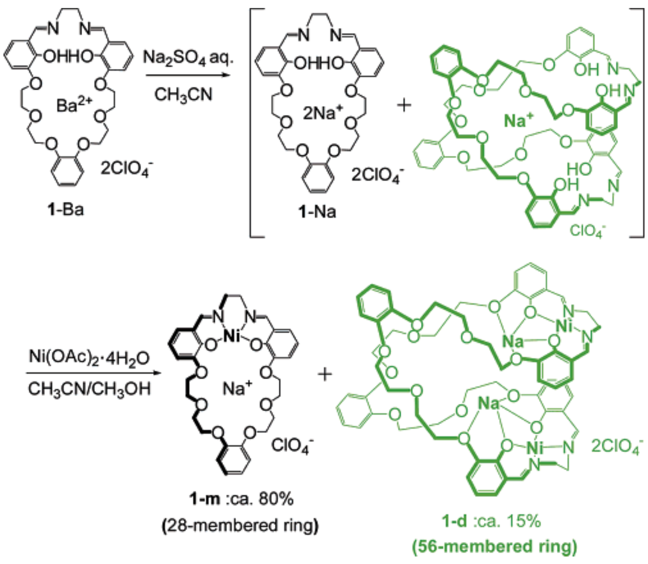
moieties. Furthermore, we describe how a [2]rotaxane, incorporating a nickel(II)−salen moiety in the macrocyclic component and two bulky stopper groups on the dumbbell-shaped unit, can be prepared when using this ring-opening-and-closing method with subsequent coordination of a metal ion.

Previously, we reported some transition-metal complexes of a macrocycle possessing a salophen unit.[6] In addition, we demonstrated the synthesis of a [2]rotaxane incorporating a palladium(II)−salophen moiety by using a threading followed by shrinking approach, which involves the threading of a rodlike unit through this macrocycle and the subsequent shrinking of the free space within the macrocycle upon coordination of its salophen moiety to a palladium metal center.[7] In that system, disassembly of the components in the absence of a transition metal could occur not only through ring opening of imino bonds in the salophen moiety but also through unthreading of the rodlike unit from the macrocycle, which was prevented by the presence of a transition metal.

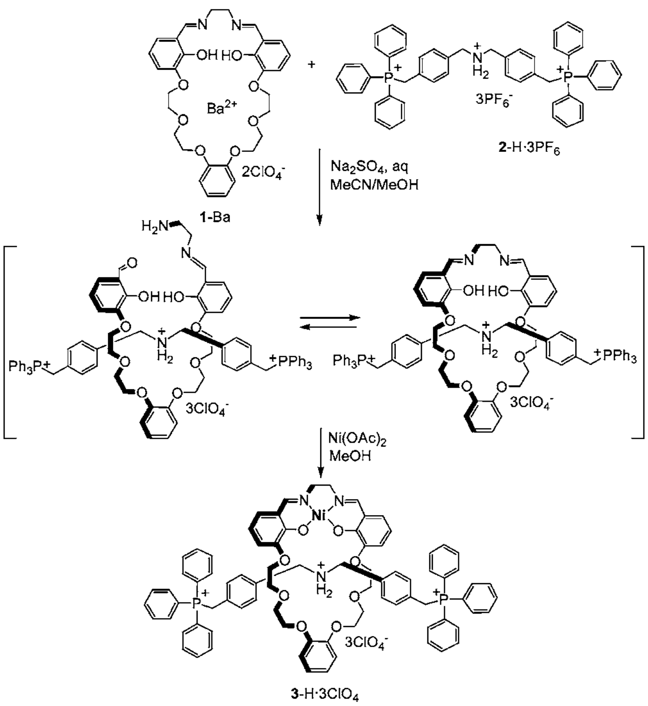
Our approach toward [2]rotaxane formation differs from that of the Stoddart group[4] in a number of respects: (1) We use metal ions to turn on and off the ring-opening-and-closing mechanism. (2) The constitution of our macrocyclic component is different (i.e., it features a salen moiety); thus, we can readily introduce a metallosalen group into the rotaxane to function as a catalytically active site, the activity of which may be controllable through modification of the bulky stoppers surrounding the metal center. (3) Stability is imparted to our rotaxane through nickel ion−salen coordination, which fixes the imino bond's lability, and not through reduction; our approach might be useful for controlling the catalytic properties through the use of different metal ions.

In this present study, we synthesized a bis-compartmental barium perchlorate−crown ether complex **1**-Ba that incorporates a salen moiety; we used **1**-Ba to obtain both the monomer **1-m** (28-membered ring) and dimer **1-d** (56-membered ring) forms of its transition-metal complexes (Scheme 1). To prohibit unthreading of the macrocycle containing the salen moiety onto the dumbbell-shaped unit, we introduced two extremely bulky triphenylphosphonium stopper groups into the latter species. The complexes formed between the salen moiety and barium(II) and nickel(II) ions were extremely stable, but in the absence of the metal, or in the presence of sodium(I), they were unstable. Upon the addition of nickel acetate, after exchanging the cation from barium(II) to sodium(I), we obtained both the monomeric and dimeric macrocycles. From this evidence for the ring opening and closing of the imine bonds of the salen moiety in the crown ether-like macrocycle, we proposed the synthesis of a [2]rotaxane possessing extremely bulky stoppers (Scheme 2). The interaction of **1**-Ba with **2**-H$\cdot$3PF$_6$, which presents terminal stopper groups, followed by the addition of aqueous sodium sulfate, led to a rotaxane intermediate in a reversible self-assembly process; the addition of nickel acetate afforded the rotaxane **3**-H$\cdot$3ClO$_4$ in reasonable yield (26%) after counterion exchange. In contrast, our attempted synthesis of a [2]rotaxane incorporating a salophen moiety, rather than a salen unit, using this ring-opening-and-closing method afforded only the transition-metal(II)−salophen complex and the unreacted dumbbell-shaped unit.[8] We have characterized the monomer **1-m**, dimer **1-d**, and [2]rotaxane **3**-H$\cdot$3ClO$_4$ through NMR and IR spectroscopic, mass spectrometric, and elemental and X-ray crystallographic analyses (Supporting Information).

Scheme 1



Scheme 2



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[6] Yoon, I.; Goto, M.; Shimizu, T.; Lee, S. S.; Asakawa, M. *Dalton Trans.* **2004**, 1513−1515.

[7] Yoon, I.; Narita, M.; Shimizu, T.; Asakawa, M. *J. Am. Chem. Soc.* **2004**, *126*, 16740−16741.

[8] This result may arise from the fact that ring opening and closing is very slow in the macrocycle incorporating the salophen moiety.

The 1D ^{1}H NMR spectra of **1-m** and **1-d** (Supporting Information, Figure S1) are considerably different, as are their 2D (ROESY and COSY) NMR spectra (Supporting Information). Most of the oligoethylene glycol protons appear as broad signals in the dimer structure (**1-d**). We observe significant downfield shifts, relative to those of the monomer, of the oligoethylene glycol protons (e_a, e_b); this phenomenon may be a result of the existence of both [C−H···O] hydrogen bonds[9] and the deshielding effects of aromatic rings. In contrast, the upfield shifts observed for the oligoethylene glycol protons *f* and *c* may be attributable to [C−H···π] interactions involving the aromatic units.

The 1D ^{1}H NMR spectrum of **3**-H·3ClO$_4$ (Figure 1c), together with its 2D (ROESY and COSY) NMR spectra (Supporting Information), provides good evidence for the formation of the rotaxane. Figure 1c indicates that the signal of the CH$_2$N$^+$ (*A*) protons in the dumbbell-shaped threadlike unit shifted downfield significantly, relative to that of the free salt (Figure 1a), presumably as a result of the formation of [C−H···O] hydrogen bonds[9] (Supporting Information). In contrast, the signal for proton *f* of the oligoethylene glycol chain of the macrocycle shifted relatively upfield; we attribute this finding to the shielding effects of the aromatic units in the thread that arises from the bent conformations of the two components (Figure 3). In addition, the signals of some of the protons in the salen units (*a*, *b*, *g*, *j*; Figure 1c) and those of the aromatic units in the dumbbell-shaped moiety (*B*, *C*; Figure 1c) shifted upfield relative to those signals in the free components; these phenomena suggest the existence of $\pi-\pi$ stacking interactions in the rotaxane.[10] Moreover, the interlocked nature of the component of **3**-H·3ClO$_4$ is suggested by the ROESY spectrum (Supporting Information), which displays cross-peaks between the signals of the protons of the ether linkages in the macrocycle (*c*−*f*) and those of both the CH$_2$N$^+$ (*A*) and aromatic (*C*) groups of the dumbbell-shaped unit.

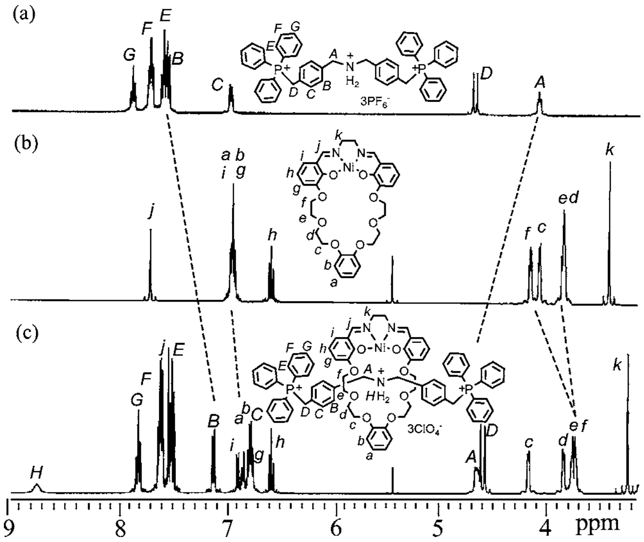

Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD$_3$CN, 298 K) of (a) the dumbbell-shaped salt **2**-H·3PF$_6$, (b) the Ni(II)−salen macrocycle, and (c) the rotaxane **3**-H·3ClO$_4$.

We obtained reddish-brown-colored single crystals suitable for X-ray crystallographic analysis upon slow evaporation of an acetonitrile solution of **1-m**.[11] The monomer structure (Figure 2a)[12] reveals a stair-shaped macrocyclic dinuclear nickel(II)−sodium(I) complex. X-ray crystallographic analysis of the orange-colored single crystals obtained upon slow evaporation of an acetonitrile solution of **1-d** revealed the dimeric structure (Figure 2b)[12] of a heterobinuclear complex formed through ring opening and closing.[13] To the best of our knowledge, this structure is the first example of a dimeric salen macrocycle based on transition-metal−alkali-metal complexation.

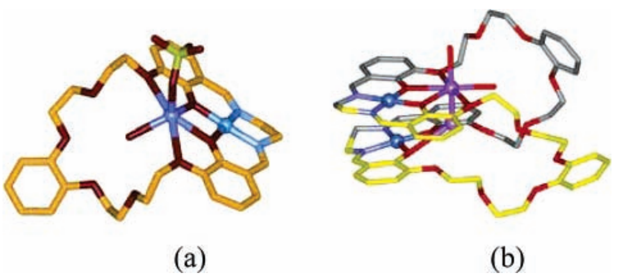

Figure 2. Solid-state structures of the (a) monomer **1-m** (28-membered ring) and (b) dimer **1-d** (56-membered ring) forms of the Ni(II)−salen macrocycle. Carbon atoms of the macrocycle are colored yellow or gray; oxygen atoms, red; nitrogen atoms, blue; nickel atoms, dark blue; sodium atoms, violet.

Furthermore, we obtained brown-colored single crystals suitable for X-ray crystallographic analysis upon the slow evaporation of a MeOH/CH$_2$Cl$_2$ solution of **3**-H·3ClO$_4$.[14] The crystal structure of **3**-H·3ClO$_4$ (Figure 3)[12] confirms that the

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[9] (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290−296. (b) Raymo, F. M.; Bartberger, M. D.; Houk, K. N.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 9264−9267. (c) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48−76.

[10] (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534. (b) Adams, H.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Spey, S. E.; Urch, C. J.; Sanderson, J. M. *Chem.−Eur. J.* **2001**, *7*, 4863−4877.

[11] Crystallographic data for **1-m**: $C_{30}H_{34}ClN_2NaNiO_{13}$, $M_r = 747.74$, monoclinic, space group $P2_1/c$, $a = 12.1529(10)$, $b = 30.119(3)$, $c = 9.3248(8)$ Å, $\beta = 112.560(1)°$, $V = 3152.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.576$ g cm^{-3}, μ(Mo Kα) = 7.86 cm^{-1}, $T = 183(2)$ K, red−brown needle, 0.40 × 0.15 × 0.10 mm, R1 = 0.0338 [$I > 2\sigma(I)$], wR2 = 0.1035 (all data), GOF = 1.068.

[12] Ball-and-stick diagrams were prepared using WEBLAB VIEWER, Molecular Simulations Inc., 2000.

[13] Crystallographic data for **1-d**: $C_{62}H_{75}Cl_2N_5Na_2Ni_2O_{28}$, $M_r = 1572.57$, monoclinic, space group $C2/c$, $a = 36.115(2)$, $b = 13.8424(8)$, $c = 30.5377(19)$ Å, $\beta = 115.058(2)°$, $V = 13\,829.4(15)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.511$ g cm^{-3}, μ(Mo Kα) = 7.23 cm^{-1}, $T = 183(2)$ K, orange plate, 0.30 × 0.20 × 0.10 mm, R1 = 0.0885 [$I > 2\sigma(I)$], wR2 = 0.2715 (all data), GOF = 1.079.

[14] Crystallographic data for **3**-H·3ClO$_4$: $C_{169}H_{186}Cl_6N_6Ni_2O_{48}P_4$, $M_r = 3640.66$, monoclinic, space group $P2_1$, $a = 18.862(3)$, $b = 22.782(3)$, $c = 19.734(3)$ Å, $\beta = 92.067(3)°$, $V = 8475(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.381$ g cm^{-3}, μ(Mo Kα) = 6.54 cm^{-1}, $T = 183(2)$ K, brown plate, 0.40 × 0.40 × 0.10 mm, R1 = 0.1234 [$I > 2\sigma(I)$], wR2 = 0.3641 (all data), GOF = 1.018.

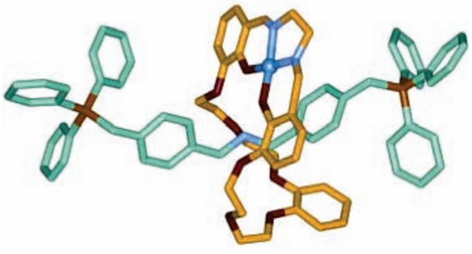

Figure 3. Solid-state structure of the [2]rotaxane **3**-H·3ClO$_4$. Carbon atoms of the macrocycle are colored gold and those of the thread are light cyan; oxygen atoms, red; nitrogen atoms, light blue; nickel atom, dark blue; phosphorus atoms, reddish brown.

macrocycle encircles the axle unit of the dumbbell-shaped moiety. Stabilization of the [2]rotaxane is achieved through a combination of (a) [N$^+$−H···O] and [C−H···O] hydrogen bonds[15] between the oxygen atoms of the macrocycle and the NH$_2$$^+$ and benzylic CH$_2$N$^+$ units of the secondary dialkylammonium ion moiety and (b) π−π stacking interactions[15] between aromatic rings (Supporting Information).

In summary, we have obtained good evidence for the ring opening and closing of the imino bonds in the salen moieties of both monomeric and dimeric nickel(II)−salen complexes. We have used this phenomenon to synthesize a [2]rotaxane incorporating a nickel(II)−salen-based macrocyclic moiety; the two bulky stopper units of the dumbbell-shaped moiety prevent threading and unthreading of the macrocycle, and thus, the formation of the [2]rotaxane must occur through a ring-opening-and-closing mechanism. We believe that this approach will be useful for the construction of other mechanically interlocked molecules and will aid in our understanding of the chemistry of salen-containing systems. In addition, such systems have great potential for use as a new class of catalytically active rotaxanes and as new tools for developing molecular devices.

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Supporting Information Available: Crystallographic data and experimental procedures for the preparation of **1-m**, **1-d**, and **3**-H·3ClO$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Gómez-López, M.; Lawrence, S. E.; Martínez-Díaz, M. V.; Montalti, M.; Piersanti, A.; Prodi, L.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 10641−10651. (b) Cantrill, S. J.; Fyfe, M. C. T.; Heiss, A. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Org. Lett.* **2000**, *2*, 61−64.