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Chiral Borromeates**

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The quest for topologically interesting molecules has led to the template-directed synthesis^[1] of a wide range of molecular catenanes and knots.^[2] Such molecules with interlocked and intertwined structures have nonplanar molecular graphs and can exhibit^[3] topological chirality.^[4] Although the classic example is the trefoil knot,^[2,4] catenanes—characterized in knot theory by the Hopf link—can also display topological chirality, provided that both rings exhibit structural directionality.^[5] By contrast, the Borromean rings (BRs)—characterized in knot theory by the Brunnian link—remain amphicheiral^[6] even after orientation. Thus, the only way by which we can render BRs chiral is to introduce chirality in the form of elements that are planar, axial, or point (stereogenic) in nature.

Although the incorporation of stereogenic centers into mechanically interlocked molecules can be inconsequential, especially if the stereogenic centers are far removed from the rest of the functional groups in the molecule, the effects of such centers can often be amplified, particularly when they are able to influence nearby molecular structure, sometimes even inducing chirality.^[7] Relatively simple transition-metal complexes containing 2,2'-bipyridyl ligands with appended stereogenic centers have been termed chirality generators (or CHIRAGENs)^[8] because the absolute configuration of these centers can determine the absolute configuration induced at the metal coordination site. This kind of chirality transfer has been identified in tight-fitting, mechanically interlocked molecules such as the catenate investigated recently by Sauvage and co-workers^[9] that contains an axially chiral binaphthyl unit. Herein, we report the preparation of two enantiomeric pairs of Borromean linked compounds^[10,11] using Zn^{II} ions to template their formation from diaminobipyridine (DAB) ligands with one of two like stereogenic

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centers (i.e., (R,R) or (S,S)) and either 2,6-diformylpyridine (**DFP**) or its 4-chloro derivative **Cl-DFP**^[12] to give the $(R)^{12}$ and $(S)^{12}$ enantiomers of the Borromean link compounds **BR**·12 TFA and **BRCl**₆·12 TFA (TFA = trifluoroacetate); that is, $(R)^{12}$ -**BR**·12 TFA, $(S)^{12}$ -**BR**·12 TFA, $(R)^{12}$ -**BRCl**₆·12 TFA, and $(S)^{12}$ -**BRCl**₆·12 TFA. It transpires that, as a consequence of introducing four stereogenic centers into each of three identical rings in these chiral Borromeates^[13] such that they pair up in locations close to the six ions, these metal ions are surrounded by chiral coordination spheres as revealed by one X-ray crystal structure and several circular dichroism (CD) spectra.

The (R,R)- and (S,S)-**DAB**-H_n $\cdot n$ TFA precursors were each synthesized (see Supporting Information) in five steps from the (R) and (S) enantiomers, respectively, of p-hydroxyphenylglycine methyl ester hydrochloride. In four separate reactions, the chiral diaminobipyridine ligands, as their TFAsalts, were treated at 70 °C for 24 h in iPrOH with equimolar amounts (0.10 mm) of either DFP or Cl-DFP, in the presence of $Zn(OAc)_2$ as the template to afford stereospecifically $(R)^{12}$ -**BR**·12TFA and $(S)^{12}$ -**BR**·12TFA, and $(R)^{12}$ -**BRCl₆·12TFA** and $(S)^{12}$ -**BRCl**₆·12TFA (Scheme 1). High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) revealed peaks at m/z 1585.3302 and 1160.2263, and 1584.2427 and 1160.1778, respectively, for the triply and quadruply charged molecular ions from $(R)^{12}$ -**BR**·12TFA and $(S)^{12}$ -**BR**·12TFA: the analogous m/z values for $(R)^{12}$ -**BRCl**₆·12 TFA and $(S)^{12}$ -BRCI₆:12TFA are 1653.5458 and 1211.9171, and 1652.5632 and 1212.4001, respectively. Although the ¹H NMR spectra of all these compounds recorded in CD₃OD at 600 MHz were characterized by broad resonances, a singlet for the 12 imine protons was discernible at $\delta = 9.0$ ppm in all four spectra and peaks for most^[14] of the other heterotopic protons in the chiral BR-12TFA and BRCl₆-12TFA compounds could be identified and assigned (Figure 1).

Single colorless crystals^[15] of $(R)^{12}$ -**BRCl₆**·12 TFA, suitable for X-ray crystallography,^[16] were obtained by vapor diffusion of Et₂O into a methanolic solution of the compound.^[17] The solid-state structure of the original, achiral Borromean rings^[10a] indicated that all three macrocycles adopt chairlike conformations, such that they confer S_6 symmetry on the molecule. In the chiral Borromean rings, we expected the C_3 axis, which is collinear with the S_6 axis in the achiral progenitor, to be present in the solid-state structure. However, although the same chairlike conformations can also be observed (Figure 2a) in the orthogonal arrangement of the three macrocycles in $(R)^{12}$ -**BRCl**₆¹²⁺, the C₃ axis is not evident: the symmetry is reduced to C_1 on account of one of the three macrocycles adopting a flipped chairlike conformation (Figure 2b). On inspection of the three chairlike conformations in $BRCl_6^{12+}$, the CH₂OH groups are oriented in pairs with the pseudo-axial and pseudo-equatorial arrangements alternating between neighboring 60° segments (Figure 3). Moreover, beyond the molecule, the packing diagrams (Figure 4) show that these CH₂OH groups result in the formation of two very different hydrophilic solvent channels that run all the way through the lattice such that the channels are lined with only pseudo-axial CH₂OH groups or only pseudo-equatorial CH₂OH groups.

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Scheme 1. Schematic representation of $(R)^{12}$ -**BR**-12TFA and $(S)^{12}$ -**BR**-12TFA, in which only the blue ring depicts all of the atoms and bonds present in the macrocycles that make up the Borromeate ring structure. By using either the (R,R)- or the (S,S)-**DAB**-H_n·nTFA ligand, enantiomeric BRs with twelve stereogenic centers are formed.

The CD spectra^[18] (Figure 5a) of the Boc-protected enantiomeric ligand precursors, (R,R)-DAB and (S,S)-DAB, constitute plots that are mirror images of each other, and both display optical activity at $\lambda < 255$ nm. Although not as simple to interpret, the enantiomeric BRs, $(R)^{12}$ -BRCl₆·12TFA and $(S)^{12}$ -**BRCl₆**·12TFA, also provide plots (Figure 5b) that are mirror images of each other. The trace from $(R)^{12}$ -**BRCl**₆·12TFA shows strong Cotton effects at $\lambda_{\min} = 224$ nm $(\Delta \varepsilon = -29.75 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1})$ and $\lambda_{\rm max} = 239 \ \rm nm$ $(\Delta \varepsilon =$ $49.0 \,\mathrm{m^{-1} \, cm^{-1}}$), most likely arising from the stereogenic centers appended to the bipyridyl ligand, considering that this higher-energy region is within the same range as the absorptions observed for the free ligand in Figure 5a. Likewise, the trace for $(S)^{12}$ -**BRCl₆**·12TFA shows intense Cotton effects in that region: $\lambda_{\text{max}} = 220 \text{ nm} (\Delta \varepsilon = 32.9 \text{ m}^{-1} \text{ cm}^{-1})$ and $\lambda_{\min} = 237 \text{ nm} (\Delta \varepsilon = -49.0 \text{ m}^{-1} \text{ cm}^{-1}).$ At lower energy ($\lambda =$ 272 nm), where the free ligand is optically inactive, a pair of antipodal CD absorptions are evident ($\Delta \varepsilon = 41.17$,

 $-27.6 \,\mathrm{M}^{-1} \mathrm{cm}^{-1}$) corresponding to $(R)^{12}$ -BRCl₆·12TFA and $(S)^{12}$ -**BRCl₆**·12 TFA, respectively. Equally interesting are the strong Cotton effects observed at $\lambda = 310 \text{ nm}$, with $\Delta \varepsilon =$ $-38.8\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ $(R)^{12}$ -**BRCl₆**·12TFA for and $\Delta \varepsilon =$ $42.6 \text{ m}^{-1} \text{ cm}^{-1}$ for $(S)^{12}$ -**BRCl₆**·12TFA. This absorption range is especially characteristic of chirality associated with the metal centers, a situation which suggests that chirality has been induced by the stereogenic centers to the zinc coordination sphere.^[19] Furthermore, the coordination spheres around the metals are themselves enantiomers of each other, as reflected by their opposing Cotton effects in the CD spectra of the enantiomeric BRs.

To eliminate the possibility that the size and shape of the Borromeate framework transmits chiral information of any form, the CD spectrum of the achiral progenitor was measured. It showed no CD response at all. As an additional verification that chirality is being induced at its metal centers, the $(R)^{12}$ -**BRCl₆**·12 TFA enantiomer was demetallated by



Figure 1. Partial ¹H NMR spectra (600 MHz) recorded in CD₃OD of a) the freshly deprotected (R,R)-**DAB**-H_n·*n*TFA ligand, b) **Cl-DFP**, and c) the (R)¹²-**BRCl**₆·12 TFA isomer. If the structure of the chiral Borromeate has C_1 symmetry in solution, then *all* the protons in the molecule are heterotopic. The observed line widths in the spectrum are consistent with this structural assignment.



Figure 2. X-ray crystal structure of $(R)^{12}$ -**BRCI**₆·12TFA viewed a) from an orthogonal perspective and b) down the core, revealing the low symmetry (C_1) resulting from one "flipped" chairlike macrocycle.



Figure 3. View of the X-ray crystal structure of $(R)^{12}$ -**BRCI**₆·12TFA down the *c* axis with pendant alternating axial (ax) and equatorial (eq) CH₂OH groups.

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tion of a recently established procedure^[13] for demetallation and reduction gives a mixture of single rings, linear fragments, and intact BRs-in this case, $(R)^{12}$ -BRCl₆H₂₄—but without the metals; that is, the Borromeands. The CD spectrum (Figure 6) of the crude demetallated chiral BRs exhibits much weaker absorptions (at the same concentrations of 8.0 µм) in the absence of the metal. In fact, only two main absorptions are apparent at $\lambda_{\min} = 248 \text{ nm} \qquad (\Delta \varepsilon = -8.09 \text{ m}^{-1} \text{ cm}^{-1})$ and at $\lambda_{\rm max} = 277 \ \rm nm$ $(\Delta \varepsilon =$ $6.61 \text{ m}^{-1} \text{ cm}^{-1}$): the first bands are within the optical activity range of the free ligand. Furthermore, the CD trace of demetallated $(R)^{12}$ -**BRCl₄H₂₄** is conspicuously lacking any absorption at 310 nm, further suggesting that chirality was induced at the metal center. These results prompted us to examine the octahedral disposition of the ligands surrounding the Zn^{II} ions from the X-ray crystallographic data (Figure 7). From this distorted octahedron, it is apparent that the chiral ligands wrap around the metal in a helical, and thus chiral, fashion.^[20] For comparison, we re-examined the X-ray crystal data for the original Borromeate and confirmed that each octahedron around the zinc in the achiral BR is an ideal octahedron with no distortion. Hence, we conclude that the presence of the nearby stereogenic centers disturbs the neighboring coordination sphere to produce chirality at metal centers in the optically active Borromeates.

reducing the 12 imine bonds. Applica-

In summary, two pairs of enantiomerically related Borromeates were synthesized stereospecifically from enantiomeric phenylglycine derivatives. All four optically active compounds have three macrocycles each containing four stereogenic centers. The one example whose crystal structure has been determined adopts an asymmetric conformation. All four compounds exhibit intense CD spectra in solution. Furthermore, the Zn^{II} octahedra, found in the X-ray crystal structure of one of the compounds, deviate substantially from ideal geometry, strongly suggesting that chirality is being transferred rather efficiently from the 12 stereogenic centers to the six Zn^{II} centers. Removal of the Zn^{II} ions and reduction of the imine bonds present in the macrocyles affords a Borromeand with a significantly different CD spectrum. In the fullness of time, the chiral Borromeates could find applications^[21] in chemical biology and materials science; or they could remain what they are presently-that is, stereochemical curiosities.

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Figure 4. Packing diagram of $(R)^{12}$ -**BRCI**₆·12TFA viewed down the *c* axis revealing alternating hydrophilic solvent channels. Depicted in the wire view are the equatorial (eq) and axial (ax) solvent channels. Hydrogen atoms, TFA counterions, and solvent molecules have been omitted for clarity.



Figure 5. Circular dichroism spectra of a) the chiral ligand precursors, Boc-protected (*R*,*R*)-**DAB** (blue) and (*S*,*S*)-**DAB** (red), both recorded at a concentration of 0.02 μm in MeOH (22 °C), b) the enantiomeric chiral BRs (*R*)¹²-**BRCl**₆·12TFA (blue) and (*S*)¹²-**BRCl**₆·12TFA (red). The CD spectrum of the achiral (unmodified) BRs was taken as a control (green). All three samples were measured at a concentration of 8.0 μm in MeOH (22 °C). Boc = *tert*-butyloxycarbonyl.



Figure 6. CD spectra of $(R)^{12}$ -**BRCI**₆-12TFA (blue) and the crude reduced chiral Borromeand (brown). Both were obtained at a concentration of 8.0 μ M in MeOH (22°C).



Figure 7. Distorted octahedron around the Zn^{II} atom, drawn from the X-ray crystal structure data (left) and its mirror image. The imine nitrogen atoms in the coordination sphere are not equivalent—one is flanked with a nearby pseudo-equatorial CH₂OH (C_{eq}) and the other is situated nearest a stereogenic center with a pseudo-axial CH₂OH (C_{ax}), thereby eliminating any planes of symmetry from the octahedron.

Experimental Section

 $(R)^{12}$ -BRCl₆·12TFA: The Boc protecting groups in (R,R)-6 were removed by the addition of neat CF_3CO_2H (0.5 mL) to (R,R)-6 (155 mg, 0.235 mmol) with stirring at room temperature for 15 min. The reaction mixture was concentrated to dryness, leaving a light pink oil. The excess of CF3CO2H was removed by two repeated addition and removal cycles of MeOH (5 mL) by rotary evaporation under reduced pressure. Any residual CF₃CO₂H was removed under high vacuum to leave (R,R)-**DAB**-H_n $\cdot n$ TFA as a pink sticky solid that is moisture-sensitive and was therefore carried onto the next step without delay. Zn(OAc)₂ (43 mg, 0.235 mmol) was added to a stirred solution (10 mL) containing (R,R)-**DAB**-H_n·n TFA (0.235 mmol) and 4-chloro-2,6-diformylpyridine (40 mg, 0.235 mmol) in iPrOH, and the reaction mixture was heated at 65 °C for 16 h to produce a pale yellow solution along with a white precipitate. The mixture was allowed to cool down to room temperature and filtered, and the precipitate was washed with *i*PrOH (3×5 mL) and Et₂O (3×5 mL). This procedure afforded $(R)^{12}$ -BRCl₆·12TFA as a white powder (117 mg). Crystals suitable for X-ray crystallography were grown by vapor diffusion of Et₂O into a solution of (*R*)¹²-**BRCl**₆·12 TFA in MeOH. Yield: 83 %; $[a]_{D}^{22} = -6.19$ (*c* = 0.2, MeOH); ¹H NMR (600 MHz, CD₃OD): $\delta =$ 4.01 (s, 24H), 6.54 (br, 12H), 6.74 (m, 48H), 8.02 (s, 12H), 8.49 (s, 12H); 9.00 ppm (s, 12H); resonances for the hydroxy protons were not observed as a result of exchange with the deuterium in the solvent. A resonance for the CH at the stereogenic center was not observed because it was obscured by the H₂O resonance; HR-ESI-MS: *m*/*z* calcd for (C₆₆H₅₂Cl₂N₁₀O₈)₃Zn₆(CF₃CO₂)₁₂: 5300.8528; found (%): 1653.5458 (90) [*M*-3 TFA]³⁺, 1211.9171 (100) [*M*-4 TFA]⁴⁺, 947.1281 (24) [*M*-5 TFA]⁵⁺, 769.9425 (6) [*M*-6 TFA]⁶⁺. (*R*)¹²-**BRCl**₆H₂₄: The Zn^{II}-containing BR complex (*R*)¹²-

BRCl₆·12 TFA (50 mg, 0.01 mmol) was dissolved in anhydrous EtOH under an Ar atmosphere at 22 °C. NaBH₄ (15 mg, 0.4 mmol) was added in one portion. The reaction mixture became cloudy immediately. It was stirred at 22 °C for 5 days. The reaction was then quenched by the addition of H_2O (5 mL), and the mixture was treated with an excess of ethylenediamine tetraacetic acid (EDTA; 175 mg) and heated under reflux for 30 min. Thereafter, the reaction mixture was allowed to cool down to room temperature and the solvents were removed under reduced pressure. The crude product was suspended in H₂O (15 mL) and filtered. The white filter cake was washed with H_2O (10 × 5 mL) to remove excess of salts and then finally with Et₂O $(3 \times 5 \text{ mL})$. This procedure afforded 26 mg of the crude product as a white solid containing both the reduced $(R)^{12}$ -BRCl₆H₂₄ and the free macrocycle in a 1.0:1.8 molar ratio, as determined from the integration of the resonances in the ¹H NMR spectrum. Therefore, this observation suggests that approximately 53% of the $(R)^{12}$ -BRCl₆·12 TFA followed a pathway in which all 12 imine bonds were reduced and the three rings remained interlocked to produce $(R)^{12}$ -BRCl₆H₂₄. The remaining 47% followed a pathway in which at least one of the rings was cleaved during the borohydride reduction to produce the two reduced macrocycles and one linear fragment. $(R)^{12}$ -BRCl₆H₂₄ and the component macrocyle mixture exhibited low solubilities in most solvents and therefore had to be used as the crude mixture. $[\alpha]_{D}^{22} = -5.1$ (c = 0.1, MeOH); selected ¹H NMR data (600 MHz, CD_3SOCD_3): $\delta = 3.59$ (s, 24 H), 3.70 (s, 24 H), 4.24 (dd, J = 4.5, 1.3 Hz, 12 H), 4.10 (bs, 12 H), 6.38 (m, 12 H), 6.70 (d, J =9.0 Hz, 24 H), 7.01 (d, J = 9.0 Hz, 24 H), 7.28 (s, 12 H), 7.46 (d, J =2.4 Hz, 12 H), 7.89 ppm (d, J = 6 Hz, 12 H) (see Supporting Information for full assignments). MALDI-MS: m/z calcd for $(C_{66}H_{60}N_{10}O_8)_3$: 1256.4; found: 1255.3 (100%) [3*M*+H+Na]⁺.

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- [13] A. J. Peters, K. S. Chichak, S. J. Cantrill, J. F. Stoddart, *Chem. Commun.* 2005, 3394–3396; we proposed therein that Borromean ring compounds that are assembled using metal ions, and that retain these metal ions as an intrinsic part of their structure, be referred to as "Borromeates". Furthermore, upon removal of

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the metal ions, the term "Borromeand" is suggested for the resulting metal-free compound.

- [14] No resonance was observed for the methine protons attached to the stereogenic centers because it was obscured by a water resonance. It was also not possible to identify one of the two vicinal protons located on the bipyridyl ligands.
- [15] Crystal data for $[(C_{66}H_{52}Cl_2N_{10}O_8)_3(ZnO_2CCF_3)_6]$ -(CF₃CO₂)₆·10.5 CH₃OH·1.5 H₂O, trigonal, a = b = 31.293(4), c = 24.348(5) Å, V = 20.649(6) Å³, space group R3, Z = 3, $\rho_{calcd} = 1.362$ g cm⁻³, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, F(000) = 8636, T = 120(2) K, 9818 unique reflections $(2\theta_{max} = 54.9^{\circ})$, of which 4944 were observed $[I_o > 2\sigma(I)]$. Absolute structure parameter = 0.0121(15). Final R factors: $R_1 = 0.1661$, $wR_2 = 0.3865$ for 611 parameters.
- [16] Single crystals of $(R)^{12}$ -**BRCl**₆·12TFA, suitable for X-ray crystallography, were obtained by vapor diffusion of Et₂O into a methanolic solution of the compound. A single colorless crystal $(0.32 \times 0.24 \times 0.185 \text{ mm}^3)$ was attached with oil to a thin glass fiber. Suitable crystals were extremely difficult to mount. Solvent loss was immediately evident as soon as the crystal was removed from the mother liquor. Data were collected on a Bruker-Nonius FR591 rotating anode diffractometer with Mo_{Ka} radiation using the phi and omega scan modes (150-second exposure per frame). Data were corrected for absorption using the SADABS program, and structure solution and refinement were performed using the SHELX-97 software package. All non-hydrogen atoms, except those in the solvent molecules and counterions, were refined anisotropically while the hydrogen atoms were included at geometrically calculated positions and allowed to ride on their parent atoms. CCDC 299519 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [17] The enantiomeric pairs of BRs, (R)¹²-BRCl₆·12 TFA and (S)¹²-BRCl₆·12 TFA, were prepared in the form of the chlorinated derivatives in order to aid the growth of single crystals suitable for X-ray crystallography. Analysis of the X-ray data supported this notion (see Supporting Information). The molecular parameters (distances, angles, etc.) are not reported here, however they are not all that dissimilar from those found in the original Borromean rings (see Ref. [10a]). The X-ray crystal structure will be discussed in more detail in a full paper.
- [18] CD Spectra were recorded on a JASCO J715 spectropolarimeter using a Xe lamp equipped with a PS-150 J power supply.
- [19] a) H.-R. Mürner, H. Stoeckli-Evans, A. von Zelewsky, *Inorg. Chem.* 1996, *35*, 3931–3935; b) H.-R. Mürner, A. von Zelewsky, G. Hopfgartner, *Inorg. Chim. Acta* 1998, *271*, 36–39; c) O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. von Zelewsky, *Chem. Eur. J.* 2001, *7*, 533–539; d) K. Campbell, C. A. Johnson II, R. McDonald, M. J. Ferguson, M. M. Haley, R. R. Tykwinski, *Angew. Chem.* 2004, *116*, 6093–6097; *Angew. Chem. Int. Ed.* 2004, *43*, 5967–5971.
- [20] a) C. J. Hawkins, Absolute Configuration of Metal Complexes, Wiley-VCH, New York, 1971; b) A. von Zelewsky, Stereochemistry of Coordination Compounds, Wiley-VCH, Chichester, 1996.
- [21] The fact that $(R)^{12}$ -**BRCl₆** 12 TFA is asymmetric in the solid state, and probably also in solution, raises an important issue namely that these kinds of BRs can exist in more than one diastereoisomeric conformation. As such, we have a necessary yet insufficient property to be able to construct molecular switches.

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