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Linking Number Analysis of a Pentadecanuclear Metallamacrocycle: A Möbius-Craig System Revealed

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An analysis of the π-electronic topology of a recently reported pentadecanuclear manganese metallacycle in terms of linking number, twist, and writhe confirms its previous assignment as a Möbius system of order six. The total degree of local torsion is reduced by a significant contribution from writhe, thus correcting the previously inferred local torsion at each metal center from 120° to ∼90°. This latter value suggests a model for the cyclic π conjugation around the metallacycle, which involves $3d_\pi-2p_\pi$ interactions at the metal center, of a type first suggested by Craig 50 years ago in the context of main group cyclic aromatic systems.

Introduction

A rectangular strip or ribbon has two surfaces and four edges, but if this object is given one half-twist (π) about its center line and the ends are joined, then a new object known as a Möbius strip is obtained, now bearing only one surface and one edge. If further half-twists are imparted before joining, Möbius strips of the *n*th order are formed, where *n* designates the number of half-twists. Interest in potentially aromatic organic molecules with Möbius topologies deriving from an electronic ribbon based on a cyclic array of 2p atomic orbitals (AOs) originated with the original suggestion in 1964 by Heilbronner.[1] Subsequent reports of the isolation of stable organic compounds illustrating this property are however few.[2] More success has recently been achieved with the focus turned to organometallic and inorganic systems. Che and co-workers have claimed a mononuclear two-coordinate Au(I) complex with a P,P donor ligand as the first characterized example of an electronic Möbius metallamacrocycle,[3] and this has recently been followed[4] by a demonstration by Kim and co-workers of a Möbius aromatic conformation ($n = 1$) induced in a range of expanded porphyrins by metalation.

Concurrently, examples of higher-order Möbius strips are starting to be identified. A strip with $n = 2$ has lemniscular (also known as figure eight) topology, and such examples abound for expanded porphyrins, with many of these also forming metallacycles.[5] Examples of organic annulenes have also been proposed.[6] Theoretical analysis has recently revealed that such twisted systems are better classified in terms of a topological property known as the linking number, L_k,[7,9] of a ribbon. L_k itself was defined in an important theorem introduced by White, Fuller, and Cãlugãreanu[10] as

$$L_k = T_w + W_r$$

For ribbons defined by a p-atomic orbital basis set, we have shown[9] that L_k must have integer values (in units of π)

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(1) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923–1928.

(2) (a) Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697–3715. (b) Herges, R. *Chem. Rev.* **2006**, *106*, 4820–4842. (c) Ajami, D.; Oeckler, O.; Simon, A.; Herges, R. *Nature* **2003**, *426*, 819–821. (d) Ajami, D.; Hess, K.; Köhler, F.; Näther, C.; Oeckler, O.; Simon, A.; Yamamoto, C.; Okamoto, Y.; Herges, R. *Chem.—Eur. J.* **2006**, *12*, 5434–5445.

(3) Kui, S. C. F.; Huang, J.-S.; Sun, R. W.; Zhu, N.; Che, C. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 4663–4666.

(4) (a) Park, J. K.; Yoon, Z. S.; Yoon, M.-C.; Kim, K. S.; Mori, S.; Shin, J.-Y.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2008**, *130*, 1824–1825. (b) Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z.-S.; Kim, K.-S.; Noh, S.-B.; Park, J.-K.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 681–684.

(5) (a) Tunyogi, T.; Deák, A.; Tárkányi, G.; Király, P.; Pálinkás, G. *Inorg. Chem.* **2008**, *47*, 2049–2055. (b) Stepien, M.; Latos-Grazynski, L.; Sprutta, N.; Chwalisz, P.; Szterenberg, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7869–7873. (c) Pacholska-Dudziak, E.; Skonieczny, J.; Pawlicki; Szterenberg, M. L.; Ciunik, Z.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **2008**, *130*, 6182–6195.

(6) (a) Rzepa, H. S. *Org. Lett.* **2005**, *21*, 4637–4639. (b) Rzepa, H. S. *Chem.Commun.* **2005**, 5220–5222.

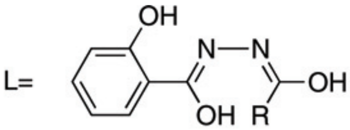
(7) Rzepa, H. S. *Org. Lett.* **2008**, *10*, 949–952.

(8) John, R. P.; Park, M.; Moon, D.; Lee, K.; Hong, S.; Zou, Y.; Hong, C. S.; Lah, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 14142–14143.

(9) (a) Rappaport, S. M.; Rzepa, H. S. *J. Am. Chem. Soc.* **2008**, *130*, 7613–7619. (b) For an earlier analysis of aromaticity in terms of electronic ribbons, see: Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193–6204.

(10) (a) White, J. H. *Am. J. Math.* **1969**, *91*, 693–728. (b) Cãlugãreanu, G. *Czech. Math. J.* **1961**, *11*, 588–625. (c) Fuller, F. *Proc. Natl. Acad. Sci. U. S. A.* **1971**, *68*, 815–819. (d) Pohl, W. *Indiana Univ. Math. J.* **1968**, *17*, 975–985.

10.1021/ic800987f CCC: $40.75



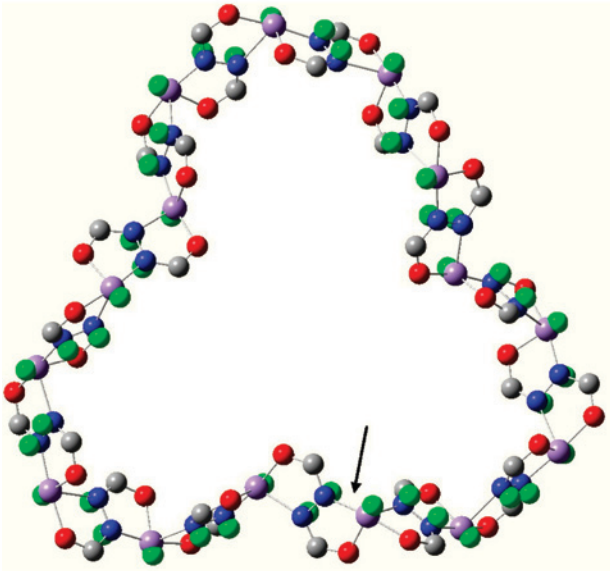


Figure 1. Schematic showing the backbone of the reported[8] C_3-symmetric pentadecanuclear metallacycle **1** (R = phenylpropioyl) with the Mn^{III} atoms in magenta (two further Mn−O ligands placed at the remaining octahedral sites are not shown for clarity, nor are the substituents on the ligands). The green spheres define the coordinates of one edge of a 0.5-Å-wide ribbon, the Mn and N atoms together the other. An arrow indicates just one of the (of the 15) 90° turns in the ribbon.

and that this value maps to the *n* referred to above. The two (noninteger) components of L_k are obtained by integration of the appropriate functions of the ribbon coordinates, with T_w being the integral of all local torsions, γ, around the center line of the basis set ribbon and W_r (known as the writhe of the system) being a nonlocal property obtained by a double integration.[9] W_r defines the extent to which the center line of the ribbon projects from 2D into 3D space. Traditional discussion of Möbius electronic ribbons[1−8] carries an implicit assumption that the center line of the ribbon is exactly bounded in 2D space and hence that W_r is zero.[11] We have shown,[9] however, that this is rarely the case, and that failure to consider any finite nonzero value of W_r (which, like L_k and T_w, can be either positive or negative) could result in a misleading analysis of T_w.

One such example is provided by a recent analysis of two hexaphyrin systems in terms of L_k and its dissection into T_w and W_r. This revealed both to be lemniscular ($L_k = 2$), one being aromatic (following an associated $4n + 2$ π-electron counting rule), the other being antiaromatic (following a $4n$ electron counting rule).[7] In each case, T_w was reduced significantly (from 2 to ~1.1) by the value of W_r (~0.9).

Recently, using the pentadentate ligand L (R = phenylpropiolyl), Lah and co-workers[8] have obtained a C_3-symmetric pentadecanuclear metallacycle, **1**, containing 15 octahedral Mn^{III} centers (Figure 1), which they claim extends characterized examples of the molecular Möbius genre to the uniquely high value of $n = 6$ ($L_k = 6$ in our terminology). Here, evaluating the values of L_k, T_w, and W_r for **1** tests this assertion.

Results and Discussion

The assignment of **1** as a "six half-twisted" Möbius strip was based on an analysis by Lah and co-workers of the local torsion angles γ at the 15 metal centers. As noted above, if W_r departs significantly from zero, this could result in a misleading conclusion. To check this, I have applied our procedure[9a] to **1**. One first needs to clearly distinguish between two types of Möbius ribbon, one based purely on a ribbon defined only by nuclear coordinates and one based on the topology of the electronic wave function (as specified by the atomic orbital basis set around the cycle).[2] Although not explicitly stated so in the Lah article,[8] the claim of Möbius topology can only refer to an electronic, and not a nuclear, band (a nuclear band would have zero width at each metal center in this case, and hence its topology would be indeterminate). The procedure involves first identifying the atomic orbital basis for constructing the ribbon, which in the case of simple cyclic annulenes is the 2p$_\pi$ AO normal to each sp^2 center. The N−N path in complex **1** provides two unique three-coordinate centers connecting a pair of Mn atoms, but the corresponding orbital on the octahedral metal center is oriented along the Mn−N σ bond. Of necessity, the orbital ribbon must therefore take a 90° turn (0.5π) at each metal atom, being approximately the torsion angle between two adjacent ligand planes for an octahedral atom. Lah and co-workers inspected the chirality along a chain of five consecutive asymmetric octahedral Mn atoms, imparted by the steric requirements of the R group, and which restrain the sequence to ΔΔΔΔΛ. Repeated three times, this accumulates 12 ~90° turns in one direction and three of ~−90° in the opposite. This however gives a total twist of only 4.5π. Lah and co-workers did indeed observe that application of this simple rule to all 15 metal centers could not recover a total twist of 6π apparently required for a "six half-twisted" Möbius strip. Instead, they somewhat arbitrarily proposed (footnote 11 of ref 8) replacing the 90° turns by 120° turns (0.667π), which does of course now sum to 6π. However, it is not obvious how an octahedral metal complex could sustain any turn of 120°, and this point was left unresolved in their article. When an orbital ribbon, constructed as above from a normal vector representing a 2p$_\pi$ AO at each N atom and a single vector oriented along one Mn−N bond (45 vectors in total, Figure 1), is subjected to a linking number analysis,[9a] the following result is obtained: $L_k = 6$, $T_w = 5.08$, and $W_r = 0.92\pi$.

The origins of the discrepancy noted by Lah et al.[8] are now revealed as mostly due to the 0.92π contribution from writhe, and smaller additional contributions from torsions at the nitrogen centers (Figure 2). Lah's conclusion that **1** is a sextuple-twisted Möbius system is nevertheless sustained, since the linking number is genuinely six!

Lah and co-workers however did not comment upon one unique feature of **1**. It is now apparent from our analysis

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(11) Wannere, C. S.; Rzepa, H. S.; Rinderspacher, C.; Ankan Paul, A.; Schaefer, H. F.; Schleyer, P. v. R.; Allan, C. S. *J. Am. Chem. Soc.* **2008**, submitted for publication.

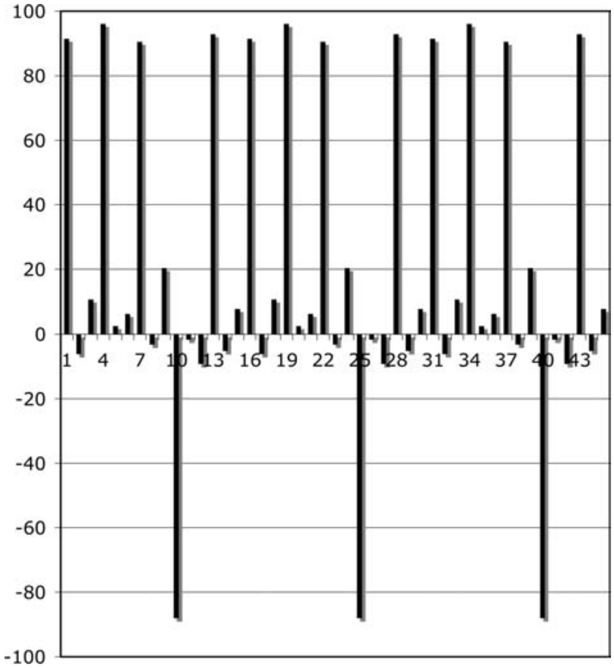

Figure 2. Local torsion angles (γ, in deg) for the 45 pairs of adjacent 2p(3d) AOs on the ring atoms in the cycle **1**, as defined by the coordinates of the ribbon shown in Figure 1. The ΔΔΔΔΛ pattern is readily detected in the torsion angles.

that almost all of the torsion is indeed due to 90° (and not 120°) turns resulting from the thrice-repeated ΔΔΔΔΛ sequence in the cycle (Figure 2). With a total of 15 metal atoms in the p_π-electron path, it might seem that the cycle comprises localized four-atom $p_\pi{-}p_\pi$ and $p_\pi{-}p_\sigma$ overlaps. Localization at each metal atom would mean it is not cyclically conjugated and hence cannot aspire to aromaticity. But in fact this cycle is not of the same type as the organic annulene systems discussed previously;[7] these were based on an electronic ribbon constructed entirely out of 2p AOs. If, instead, a 3d AO replaces the 2p AOs at each Mn center, we have a type of Möbius system first noted by Craig and Paddock some 50 years ago,[12] and which naturally allows conjugation to be maintained across the metal center with a 90° turn. Precedent for participation of a C−M σ bond in cyclic aromatic conjugation is well established for many metals[13] and even extends to nonmetals such as silicon.[14]

Conclusions

The identification of 3d/2p AO conjugation in Möbius aromatic cycles would be original, as would the Craig−Möbius motif itself in such a large metallacycle, an idea that appears to have been largely disregarded since its original suggestion.[12] Although the pattern of unequal numbers of Δ and Λ octahedral chiralities in a metallacycle has thus far only been identified in **1**, it would be desirable to have further examples of such Möbius−Craig metallacycles and to establish the relationship of this unusual orbital topology to any aromaticity or associated properties sustained by this type of cycle.

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(12) (a) Craig, D. P.; Paddock, N. L. *Nature* **1958**, *181*, 1052–1053. (b) Craig, D. P. *J. Chem. Soc.* **1959**, 997–1001.

(13) Two examples suffice: (a) M = Mg: Wehmschulte, R. J.; Twamley, B.; Khan, M. A. *Inorg. Chem.* **2001**, *40*, 6004. (b) M = Mn: Solari, E.; Musso, F.; Gallo, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 2265.

(14) Choi, N.; Lickiss, P. D.; McPartlin, M.; Masangane, P. C.; Veneziani, G. L. *Chem. Commun.* **2005**, *48*, 6023–6025.