Linking number analysis of a self-assembled lemniscular Möbius-metallamacrocycle†‡

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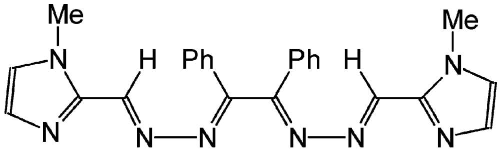
A 26 membered, 24π-electron metallamacrocycle containing two Ag(I) centers is shown to be a double-twist Möbius cycle by a linking number analysis.

A rectangular strip of paper has two surfaces and four edges. But if it is given a half-twist (180°) along its axis and the ends are joined, then an object with one side and one edge is obtained which is known as a Möbius strip. It has many unusual properties which have attracted mathematicians, artists and chemists for many years.[1–4] The same strip can be given further half-twists, generating a general class of objects known as "paradromic" rings, which can also be referred to as Möbius strips of the *n*th order, where *n* designates the number of half-twists. A paradromic figure has only one surface for odd values of *n*, but two for even values. Paradromic objects are also dissymmetric (chiral) and in idealized molecular form will belong to the C_2 or D_n symmetry point groups.

The occurrence of electronic Möbius topologies with $n = 1$ has been argued theoretically with respect to many organic aromatic molecules since the original suggestion by Heilbronner[4] in 1964. It has also been suggested for the transition states of many pericyclic reactions proceeding with (idealized) C_2 symmetry.[5] However, reports of the isolation of related stable compounds are very few.[2,3,6,7] Möbius strips with both $n = 1$ and $n = 2$ of single crystals of $NbSe_3$ have been reported,[8] although this description relates to the morphology of the crystal rather than to its electronic properties. Metallo-organic chemists are not lagging behind. Che and co-workers have very recently proposed that a mononuclear 2-coordinate Au(I) complex of a P,P donor ligand is the first example of an electronic Möbius metallamacrocycle[9] and Osuka, Kim and co-workers[10] have demonstrated how Möbius aromaticity ($n = 1$) is induced in a pentaphyrin by Rh(I) metallation. Characterization of a paradromic inorganic complex with six half-twists has been claimed very recently.[11]

A Möbius strip with $n = 2$ has figure-eight or lemniscular topology. There are a number of metallo-organic examples of such lemniscular systems,[12] including a class of molecule known as the octaphyrins, where lemniscular examples abound. Theoretically, possibilities of finding purely organic counterparts do exist.[2,3,13,14] In 2005, one of us suggested that the "*characterization of stable molecules exhibiting…even higher order Möbius twists is…a tantalizing possibility.*"[2] More recently it has been shown that such systems are more formally classified in terms of a property known as the linking number L_k, this having the same integer value (in units of π) as the *n* referred to above,[15] but comprising the sum of two further components known as T_w (the sum of all local twists) and W_r (a non-local property known as the writhe of the system). Both T_w and W_r are independent chiral indices, and can be either positive or negative. A recent analysis of two hexaphyrin systems in terms of L_k and its components revealed both to be lemniscular ($L_k = 2$), one being aromatic and following an associated $4n + 2$ electron counting rule, and the other being anti-aromatic and following a $4n$ electron counting rule.[16] Herein we report a putatively lemniscular metallamacrocycle which has been obtained through self-assembly, and an analysis of its structure, its linking number L_k and its potential for aromaticity. Ascertaining aromaticity in molecules with ribbon like topologies was originally proposed in 1971;[17] our approach[15] augments this by computing the topological linking number, twist and writhe of the ribbons.

For quite some time we have been working on metal complexes of helical ligands. The results have been encouraging. We have been able to generate mononuclear double helical complexes of a large metal ion such as Cd^{2+}.[18,19] In one of them, the metal ion is square planar.[19] So far, no other helical complex is known where the metal ion is square planar. We have been exploiting the N=C(Ph)–C(Ph)=N twist of benzil dihydrazone[20] to design helical N donor ligands. Our present ligand system L is the 1 : 2 condensate of benzil dihydrazone and 1-methyl-2-imidazole carboxaldehyde.[19] The N=C(Ph)–C(Ph)=N torsion angle in L in the solid state is ~106°, very different from that observed in benzil dihydrazone which is ~70°.



ligand L

Reaction of hydrated $AgClO_4$ with L in acetonitrile in equimolar proportions at room temperature yields a yellow

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crystalline compound $[Ag_2L_2](ClO_4)_2\cdot 0.5H_2O$ (**1**). The X-ray crystal structure of the cation is shown in Fig. 1(a). The two silver atoms are both 2-coordinate being bonded to two imidazole nitrogens, one from each ligand. Consequently a 26-membered metallamacrocycle is generated. Bond lengths are Ag(1)–N(11) 2.259(4), Ag(1)–N(58) 2.189(4) Å and Ag(2)–N(28) 2.141(4), Ag(2)–N(41) 2.160(4) Å. A search of the Cambridge Structural Database reveals that 2-coordinate Ag^+ (of which there are ~20 acyclic examples) exhibits single Ag–N bond lengths in the range 2.2–2.3 Å. The angles subtended at the metal atoms are very different at 131.9(1) and 164.6(1)°. The two silver atoms are not bonded at a distance of 4.169(1) Å. The next closest distances of other nitrogen atoms to the silver atoms are Ag(1) to N(17) at 2.583(4) Å and N(52) at 2.815(4) Å and from Ag(2) to N(47) at 2.789(5) Å, and to N(22) at 2.981(2) Å but these can only be considered as weak interactions. As expected the N(18)–C(19)–C(20)–N(21) and N(48)–C(49)–C(50)–C(51) angles are *gauche* at 92.3(6) and 88.8(5)°, respectively. The other torsion angles show that the constituent parts of the ligands are relatively coplanar although the twist around the N–N bonds should be noted, being 145.5(4) and 143.2(4)° in the two ligands, respectively. The metalla-macrocycle has no imposed crystallographic symmetry but it does exhibit 2-fold symmetry in solution, as is evident from the ^1H NMR spectrum of **1**, with no fluxional behaviour apparent.

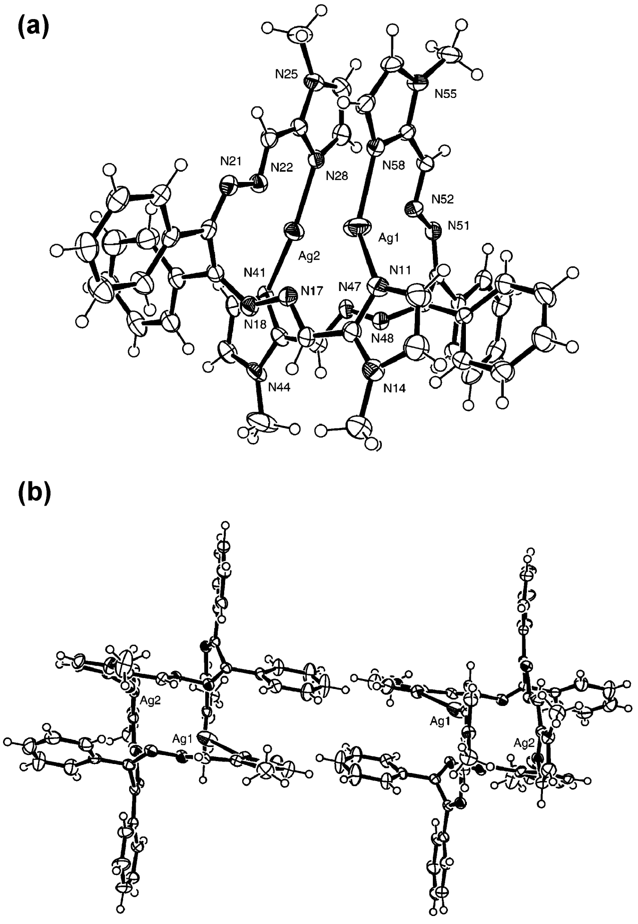


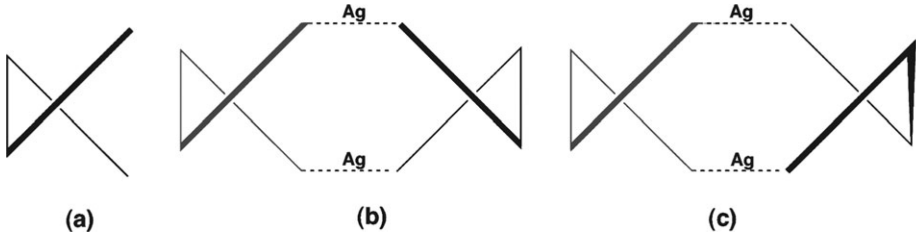
Fig. 1 (a) The structure of the cation $[Ag_2L_2]^{2+}$ in **1** with ellipsoids at 50% probability. (b) The two molecules of **1** with different chirality related by a centre of symmetry in the triclinic unit cell.

Our helically chiral ligand L can be schematically represented by structure (a) in Scheme 1, which shows that stitching together two such entities by a 2-coordinate metal ion such as Ag(I) can be done in two ways. The heterochiral mode (b) employs two ligands of opposite chirality to produce a *meso* complex with a plane of symmetry. The homochiral mode (c), which yields a chiral complex with two-fold axes of symmetry, is the one adopted by our metallamacrocycle in **1**. Fig. 1(b) shows that the unit cell contains both the enantiomers of **1**, confirming the chirality of our system.

We now present a computational analysis of this system. The geometry of the $[Ag_2L_2]^{2+}$ cation in **1** was subjected to density functional energy optimization using the B3LYP/cc-pVDZ procedure [a cc-pVDZ-pp (pseudopotential) basis[21] was employed on the Ag centres].[22] Freed of the perturbing counterions and solvent, the significant asymmetry in the crystal structure changed to higher D_2 symmetry, a normal mode analysis showing this to be a true minimum with only positive computed force constants. Comparison of the crystal and computed structures is illustrated in Fig. 2.

Whilst the computed bond lengths are in overall good agreement with the crystal structure, several geometric features merit a special mention. The separation of the carbons bearing the phenyl substituents (1.514 Å) are very close to single bonds in length; the N–C–C–N torsion angle (104_{calc}/91°) at this bond is close to π-orthogonality (Fig. 2). This clearly suggests that the cyclic p_π–p_π conjugation around the annulene periphery of the metallacycle is largely interrupted at these two positions (at least). The remaining bonds show evidence of significant short/long bond alternation, typical of a non-aromatic system with localized double bonds. The Ag–N bond lengths show some slight evidence of being shorter than normal single bonds (*vide supra*). To estimate any double bond character which might indicate p_π–p_π interaction between the N_{2p} and Ag_{5p} atomic orbitals, an NBO analysis was carried out.[23] This reveals an Ag_{5s} population of 0.39 electrons, an Ag_{5p} population of 0.13 and a total NAO bond order at each Ag^+ of 1.094, indicating significant ionic character. Of the interactions between the Ag^+ 5p orbitals as acceptors [designated LP*(7/8)Ag], the E(2) terms with the adjacent nitrogen atoms as donors are small (1.3/2.1 kcal mol^{-1}), dwarfed by the interaction into the 5s orbital [LP*(6)Ag] of 43.3 kcal mol^{-1}. This suggests that p_π–p_π conjugation across the Ag atoms is also small, and that cyclic conjugation across the macrocycle as a whole is negligible.

To recapitulate the selection rule noted above, a ground state singlet annulene will only be conjugated and hence potentially aromatic if its cyclic p_π-ribbon sustains an even (or zero) value for the linking number L_k and if the resulting molecular orbitals are populated with $4n + 2$ electrons.[13] If the π-MOs are instead populated with $4n$ electrons, then potential aromaticity only results if L_k is odd. These two rules can be reversed for anti-aromaticity; thus a $4n$ system with an even L_k will be anti-aromatic (or merely non-aromatic), as will a $4n + 2$ system with an odd L_k. The D_2 symmetry of **1** is only compatible with even values of L_k (2, 4 *etc.*); odd values would require C_2 or D_3 symmetries. We have verified this postulate



Scheme 1

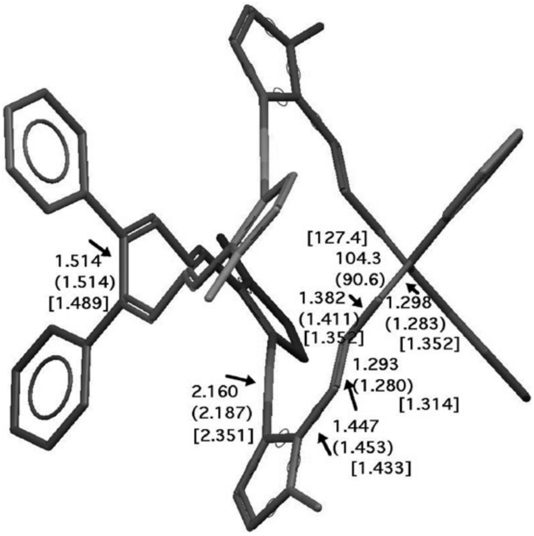


Fig. 2 B3LYP/cc-pVDZ/cc-pVDZ-pp computed (mean X-ray) [two-electron reduced version of **1**] bond lengths (Å) and the central N–C–C–N torsion angle (°) for **1**; hydrogens are not shown for clarity. The orientation of the molecule is as represented in Scheme 1. Full computed details are available *via* the following digital repository entries: http://dx.doi.org/10042/to-603 for **1** and http://dx.doi.org/10042/to-607 for the two-electron reduced version.

by analysing the π-ribbon topology of **1** in the manner previously described,[15] and have obtained the following values; $L_k = 2$, $T_w = +2.47$, $W_r = -0.47\pi$. If the experimental geometry is used, the values are $L_k = 2$, $T_w = +2.78$, $W_r = -0.78\pi$, the difference being due to perturbation in the solid state by *e.g.* the perchlorate counterion. This is the first identified example of a real system where the signs of T_w and W_r are opposed, and for which the writhe actually reduces the degree of p_π–p_π conjugation in the metallacycle by increasing the total T_w.

As noted above, **1** is a 26-membered metallacycle, but two of those atoms are in fact Ag^+, and hence carry no contribution to the total p_π-electron count, rendering **1** a 24π-electron 4*n* system ($n = 6$). Since L_k is now formalized as an even integer, one can also formally infer that **1** must be a 4*n*-electron anti-aromatic species. However, such anti-aromaticity is largely eliminated by localizing a significant proportion of the 2.47π of total twist into two orthogonal locations in the ring, rendering it merely a non-aromatic system. The NICS(0) value at the centroid is computed to be −0.2 ppm, a typical value for a non-aromatic system.[24,25]

Might there be a mechanism to invert the anti (non) aromaticity of **1**? A simple expedient (unfortunately possible for **1** only *via* computation) is a 2-electron reduction of the dication to a neutral, and hence a $4n + 2$ electron system. This does appear to be more delocalized; thus the relevant C–C length decreases from 1.514 to 1.489 Å, and the N–C–C–N torsion angle at this point increases from 104 to 127° (Fig. 2) reducing the orthogonality in this region. The computed NICS(0) indicates a slight trend towards aromaticity (−1.7 ppm). The degree of bond alternation around the ring also reduces but the values $L_k = 2$, $T_w = +2.53$, $W_r = -0.53\pi$ reveal that the total twist T_w actually increases slightly compared to the values for the computed dication (+2.47, $W_r = -0.47\pi$). It has previously been shown that these parameters are relatively insensitive to the aromaticity or anti-aromaticity of rings based on a hexaphyrin core comprising only a carbon/nitrogen periphery,[16] but there are as yet no other analyses for rings containing metals such as the Ag in **1**.

The overall conclusion from the linking number analysis applied in this article is that compound **1**, as a 4*n*-electron metallacyclic annulene, avoids formal double-twist Möbius anti-aromaticity by the presence of essentially orthogonal torsions in the ring and exhibits writhe which accentuates rather than attenuates the local torsions. This implies that there may be ample scope for optimizing the properties of such complexes for greater stability and aromaticity.

Experimental

General

Microanalyses were performed using a Perkin-Elmer 2400II elemental analyzer. FTIR spectra (KBr) were obtained on a Shimadzu FTIR-8400S spectrometer and 300 MHz NMR spectra (reference: TMS) on a Bruker DPX300 spectrometer.

Syntheses

L. L was prepared as reported elsewhere.[19] Its NMR data are reproduced here from the previous report[19] for ready reference. ^1H NMR ($CDCl_3$) δ/ppm: 3.49 (s, 6H, methyl), 6.86 (s, 2H, imidazole), 7.11 (s, 2H, imidazole), 7.26–7.89 (10H, aromatic), 8.58 (s, 2H, =CH). ^{13}C NMR ($CDCl_3$) δ/ppm: 35.93 (methyl carbons), 141.80 (quaternary carbon of imidazole), 133.64, 167.79 (other 2 quaternary carbons), 153.00 (CH=N), 125.94–131.37 (other 5 carbons).

$[Ag_2L_2](ClO_4)_2 \cdot 0.5H_2O$ (1). $AgClO_4 \cdot xH_2O$ (40 mg) dissolved in 5 ml of acetonitrile was added dropwise to a 10 ml acetonitrile solution of L (84 mg, 0.2 mmol) with stirring. The resulting bright yellow solution was stirred for 3 h. Then 5 ml of toluene was added to it and left for slow aerial evaporation. A bright yellow crystalline compound that appeared after two days was filtered, washed with a few drops of methanol and dried in air. Crystals suitable for X-ray diffraction were obtained from this sample. Yield: 100 mg (80%). Anal. calcd for $C_{48}H_{45}N_{16}Ag_2Cl_2O_{8.5}$: C, 45.40; H, 3.60; N, 17.60%; found: C, 45.21; H, 3.50; N, 17.73%. FTIR (KBr) ν/cm^{-1}: 625 s, 1094 vs (ClO_4). ^{1}H NMR (CD_3CN) δ/ppm: 3.84 (s, 12H, methyl), 6.93 (s, 4H, imidazolyl), 7.32–7.52 (24 aromatic protons), 8.47 (s, 4H, N–N=CH). ^{13}C NMR (CD_3CN) δ/ppm: 33.62 (methyl carbons), 141.16 (quaternary carbon of imidazole), 132.68, 164.66 (other 2 quaternary carbons), 149.034 (CH=N), 126.85–131.01 (other 5 carbons).

X-Ray crystallography

13902 independent data were collected for **1** with MoKα radiation using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analysis was carried out with the Crysalis program.[26] The structure was solved using direct methods with the SHELX97 program.[27] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program.[28] The structure was refined on F^2 using SHELX97.[27]

Crystal data. $C_{48}H_{45}N_{16}O_{8.5}Cl_2Ag_2$, M_w = 1268.64, triclinic, space group $P\bar{1}$, a = 12.6647(8), b = 14.9762(8), c = 15.2718(10) Å, α = 74.519(5)°, β = 83.036(5)°, γ = 68.151(6)°, U = 2590.2(3) Å^3, Z = 2, μ = 0.930, D_c = 1.627 g cm^{-3}, R_{int} = 0.0306, R_1 = 0.0740, wR_2 = 0.1432 for 9610 observed reflections and R_1 = 0.1124, wR_2 = 0.1598 for all data.

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