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First examples of bispidine-ferrocene cyclophanes ☆

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ABSTRACT

Two approaches for the syntheses of bispidine-ferrocene cyclophanes were reported. Both include the acylation of 1,5-dimethylbispidin-9-one (H_2Bp) or its pendant amino-armed derivative by 1,1'-ferrocenoyl ($Fc(CO)_2$) dichloride. The first approach allowed to isolate di-, tri- and pentameric cyclic oligomers of composition $(BpFc(CO)_2)_n$. The second one included the preliminary functionalization of H_2Bp by N-protected glycine followed by deprotection and cyclization with $Fc(COCl)_2$. The crystal structure of two new bispidine-ferrocene cyclophanes was established by single-crystal X-ray study. This study revealed the anti-conformation of amido-groups attached to the bispidine nitrogen atoms for both molecules. Various NMR techniques were applied to study the solution behavior of the macrocycles; the predominant anti-conformation in solution was also proved. The acyclic model compound $Bp(FcCO)_2$ also showed only anti-conformer as revealed by VT-NMR and X-ray studies. Cyclic voltammetry study showed the difference in oxidation potentials of the Fc moiety within the row $Bp(FcCO)_2$ – $(BpFc(CO)_2)_2$ – $(BpFc(CO)_2)_3$ with splitting of the oxidation curve in two later cases. The results obtained in this work will find an application in design and study of novel bispidine-ferrocene cyclophanes for the purposes of supramolecular sensing and catalysis.

1. Introduction

The chemistry of macrocycles is in the heart of supramolecular chemistry [1]. Macrocycles are important because they exhibit various types of receptor activity, act as selective sensors, components of supramolecular machines, and versatile models for study the conformational transitions [2–4]. The incorporation of new building blocks in the macrocyclic core leads to unexplored types of activity, selectivity and, in general sense, widen the habitual frames of our knowledge about the Nature.

3,7-Diazabicyclo[3.3.1]nonanes (aka bispidines) belong to the class of widely used diamines because of their unique conformational, coordination and biological properties [3,5–10]. Ferrocenes are also important class of organometallic compounds with well-known electrochemistry, photochemistry and biological properties [11–14]. It looks promising to conjugate two different valuable fragments – bispidine and ferrocene – in one macrocyclic molecule, that would allow one to design and explore novel, with great extent of unusual, supramolecular properties, i.e. as redox-sensors to cations [15]In the frames of our general interest in bispidine chemistry [16] and application of bispidine-like molecules to the synthesis of supramolecular architectures [17], we became interested in making macrocycles combining complexing ability of bispidine and redox activity of ferrocene.

No more than 10 bispidonophanes, i.e. macrocycles containing at least one bispidine fragment, are known in literature. Concerning the ferrocenophanes, i.e. macrocycles possessing at least one ferrocene unit, we may say that this chemistry is much more studied [2,18-20].

In this paper, we describe for the first time the synthesis and structural study of bispidine-ferrocene cyclophanes (BFC). As the first synthetic approach, we choose one step acylation of 1,5-dimethyl-3,7-diazabicyclo[3.3.1]nonane-9-one (**1**, hereafter bispidine) or its 1,3-diazaadamantane analogue because this reaction proceeds quickly at room temperature. The second approach to the bispidine-ferrocene cyclophane uses the acylation of preliminary formed pendant amino-armed bispidine derivative by 1,1'-ferrocenoyl dichloride. The structural and conformational features of the amide bond formed during the synthetic stages gave some additional interesting items to the discussion of the results. Indeed,

☆ This paper is dedicated to the 70th anniversary of Prof. E.S. Shubina.

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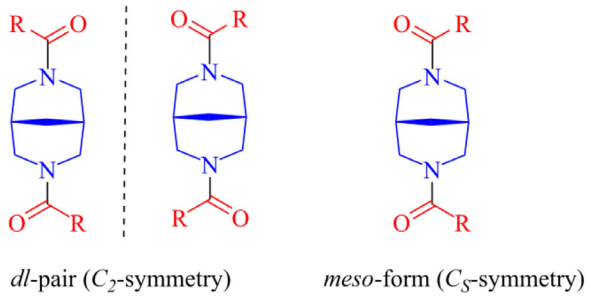


Fig. 1. The stereochemistry of bispidine bis-amides: the dl-pair, where two carbonyl oxygens are in anti-position (left); the meso-form, where those two atoms are in syn-position (plane of symmetry, right).

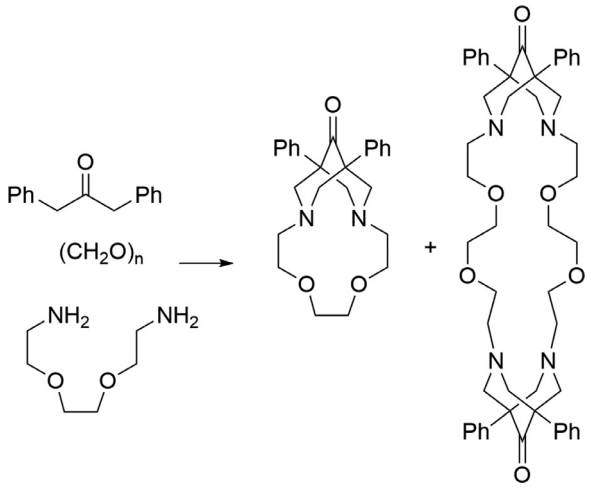
it is well-known in bispidine's bis-amide chemistry that at room temperature both anti- and syn-stereoisomers (Fig. 1) could be observed using NMR spectroscopy in some solvents [3,21,22].

2. Results and discussion

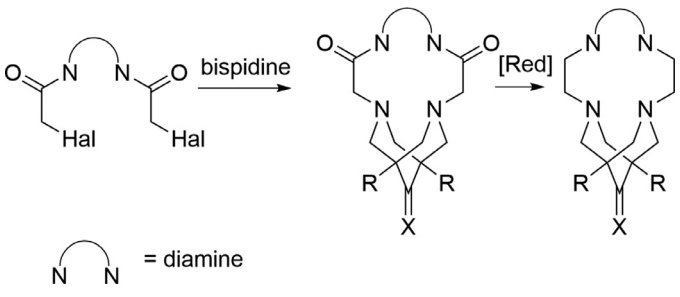
2.1. Known ways to bispidinophanes

There are three general approaches to bispidine-containing macrocycles.

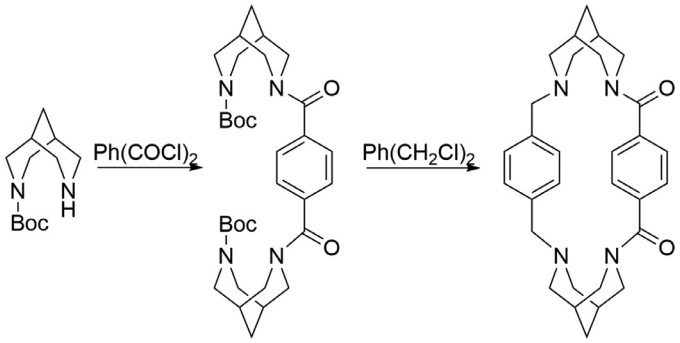
(i) Mannich condensation with appropriate diamines [23-25] (Scheme 1) typically leads to macrocycles in one step but with very low yield.
(ii) Sequential acylation and alkylation potentially lead to asymmetric macrocycles with different bispidines or diamines (Scheme 2) but the linkers are always polyalkyl chains.



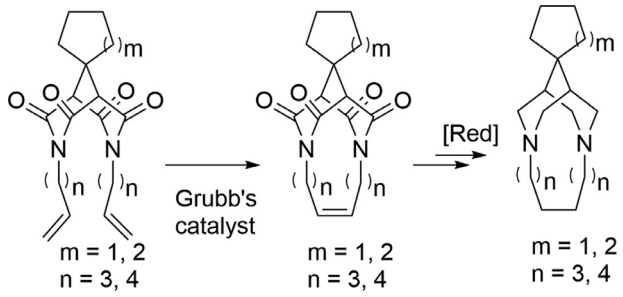
Scheme 1. Azacrown bispidine synthesis based in Mannich condensation [23].



Scheme 2. Tetrazabispidine macrocycles by acylation-alkylation-reduction sequence. X = H_2, O, $CHCO_2Et$, R = H, CH_3, Ph [26-32].



Scheme 3. Bispidine macrocycle with asymmetric linkers by acylation-alkylation sequence [33].



Scheme 4. Bispidine macrocycles by RCM [35].

(iii) Also, a modular approach can be applied to make the bispidine macrocycles with different linking groups [33,34] (Scheme 3).
(iv) Ring-Closing Metathesis (RCM) reaction is used for macrocycle closure when two alkene terminal groups are present [35] (Scheme 4) in the precursor. This method typically gives up to 36-80% yields.

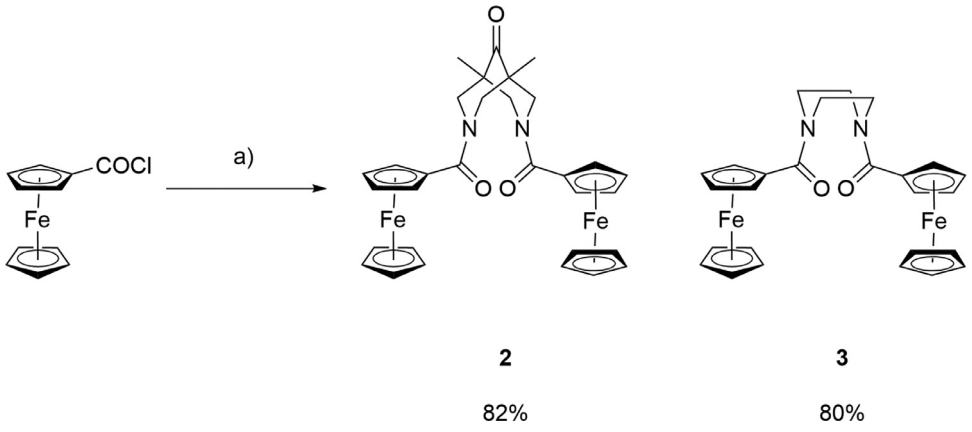
Only one paper reports on the acyclic conjugates of bispidine and ferrocene [36]. To the best of our knowledge, no ways to bispidinophanes based on the simultaneous formation of two bonds in one reaction step are present in literature. Thus, we attempted to use the amidation of bispidine building blocks by ferrocenoyl dichloride.

2.2. Synthesis

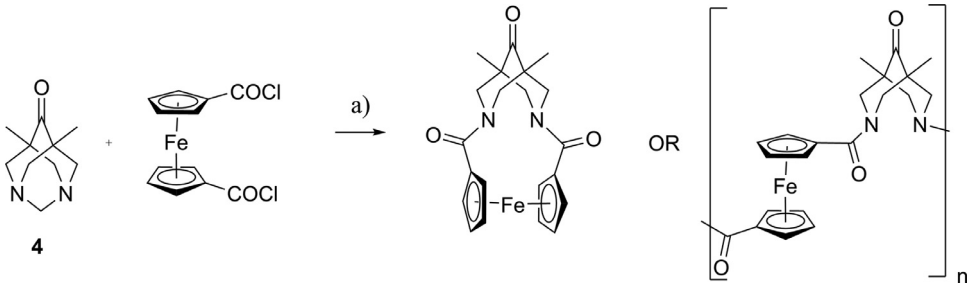
To compare the stereochemistry and to study the effect of macrocyclic structure, we synthesized model acyclic compounds **2** and **3** (Scheme 5).

As the first attempt for cyclophanes making, we tried simply looking methylene bridge-splitting reaction of 5,7-dimethyl-1,3-diazaadamantan-6-one (**4**) with 1,1'-bis(chlorocarbamoyl)ferrocene to make the smallest possible macrocycle of this series (Scheme 6). But the product was insoluble in any solvent making it impossible to analyze it thoroughly. Presumably, the bispidine-ferrocene containing polymeric product(s) were formed in this reaction instead of the desired monocycle which seems to be highly strained molecule (Scheme 6).

Taking in consideration the failure in the reaction with diazaadamantane **4**, in another attempt we applied high dilution conditions and slow addition of diamine 1 to the solution of chloroanhydride and triethylamine in toluene, and this way was successful. Three compounds were separated with column chromatography, dimer **5c²**, trimer **5c³** and pentamer **5c⁵** (scheme 7). The size of macrocycles were confirmed by HRMS-ESI (see SI), while their ^{1}H-NMR spectra were almost identical.



Scheme 5. Synthesis of model acyclic ferrocenoyl diamines: (a) bispidinone **1** for **2** or piperazine for **3**, Et_3N, toluene, 20°C.



Scheme 6. Bridge-splitting reaction. (a) $NaHCO_3$, C_6H_6, H_2O, 20°C, 2 h.

The second approach to BFC was to combine the N,N'-functionalized bispidine **S4** with ferrocenoyl moiety (Scheme 8).

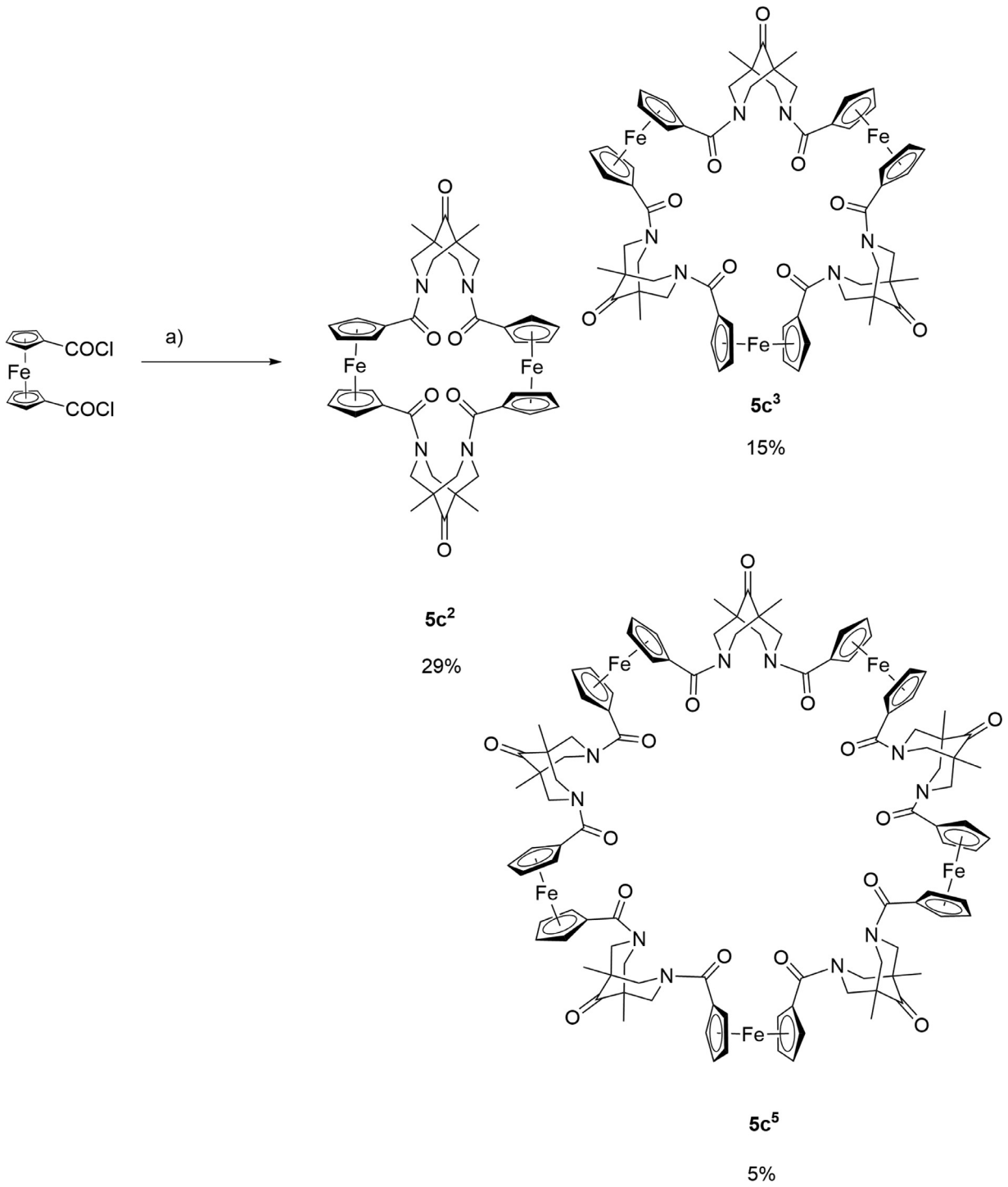
BFC **6** was synthetized by the same reaction (compare Schemes 7 and 8) but in somewhat different conditions, however, the yield was also low because of flexibility of molecule **S4**. The attempt to use the opposite reagent design, i.e., amidation of bispidine with bis-alanine-functionalized ferrocene failed, presumably due to flexibility of ferrocenic component of the reaction.

2.3. X-Ray diffraction study

The structure of **2** contains one crystallographycally independent molecule lying on general position (Fig. 2). The asymmetric unit of formally 20-membered metallocycle **5c²** comprises of two independent molecules with very close geometrical parameters (Figs. 3, 4), one solvate ether molecule, and one solvent chloroform molecule disordered over three proximal positions.

In all structures, bispidinone skeleton adopts chair-chair conformation with N…N separations ranging within 2.856 – 2.887 Å. Both molecules adopt in crystal state the anticonformation in respect to both carbonyl fragments attached to the bispidine's nitrogen atoms. The main geometrical parameters of bicyclic core in studied compounds are close to the values reported and discussed for several bispidine derivatives in [37, 38] and references cited therein. All amide fragments $(CH_2)_2$N-C(=O)-C are planar within 0.16 Å. In all cases two amide substituents at each bispidine framework adopt mutual anti-conformation. Both molecules **2** and **5c²** contain sandwich ferrocenyl fragments with typical Fe-C distances (CSD ver 5.39, [39]). In both **2** and **5c²**, all ferrocenyl fragments adopt staggered conformation with m=3 [40, 41]. Both macrocyclic molecules of **5c²** contain central holes. Unfortunately, the size of these holes is too small to accept any guest molecules (the separations of some opposite carbonyl oxygen atoms are less than 4 Å). No short intermolecular contacts were observed in the studied crystals.

The asymmetric unit of the crystal of **6** (Fig. 5) contains a chloroform molecule and the macrocycle, which has almost a regular ferrocene structure with two short linkers to the bispidine fragment, formally forming a 16-membered macrocycle. The Cp planes are parallel: the Cp..Cp folding angle is 0.75(13)°, and the centroid(C13..C17)-Fe-centroid(C21..C25) angle is 178.3°. The Fe atom is entirely symmetrically bounded to the Cp ligands, since the Fe-$Cp_{centroid}$ distances and normals from Fe to the Cp plane are equal within the ESDs: 1.649(2)Å for Fe-Cp(C13..C17) and 1.647(2)Å for Fe-Cp(C21..C25). Due to rather short (four-membered) chains from ferrocene to rigid bispidine, the C_{Cp1}-$centroid_{Cp1}$-$centroid_{Cp2}$-C_{Cp2} torsion angles for the closest carbon atoms of two different Cp ligands lie in the range of 16.1° to 16.3°, and the C13-centroid(C13..C17)-centroid(C21..C25)-C21 torsion angle is 56.2°. Therefore, the Cp carbon atoms adopt a conformation somewhere between staggered and eclipsed. The short linkers between ferrocenyl and bispidine moieties, which additionally contain π-π (Cp-CO-NH) and p-π (>N-CO) conjugated fragments, sterically induce short range of non-covalent intramolecular interactions, e.g., the N1..N2 distance is 2.832(6)Å, the C10..C18 bond length is 3.300(6)Å. In order to reduce intramolecular repulsion between the linkers and to partly relax the steric strain of the macrocycle, one of the linkers (atoms C12, O2, N3, C11, C10 and O1) is significantly bent, whereas the other linker (C20, O4, N4, C19, C18 and O3) is approximately flat and is located almost within the Cp plane (C21..C25). The following geometrical parameters support this idea: the (C1, N1, C4, C10, O1)-(C3, C6, N2, C18, O3) dihedral angle deviates significantly from 0°, being equal to 21.05(12)°; atoms C20, O4 and N4 lie nearly within the Cp plane (C21..C25), but atoms O2 and N3 deviates significantly from the other Cp plane (C13..C17) by 0.308(9)Å and 0.28(1)Å, correspondingly; the dihedral angle



Scheme 7. BFC's by bispidinone acylation. (a) bispidinone **1**, Et_3N, toluene, 20°C.

between planes defined by the atom sets C12, C13, O2, N3 and C13..C17 is 14.9(2)°, but the (C20, C21, O4, N4)-(C21..C25) dihedral angle is 2.25(14)°; the folding angles (C1, C2, C4, C5)–(C1, N1, C4, C10, O1) and (C2, C3, C5, C6)–(C3, N2, C6, C18, O3) are 39.3(2)° and 51.3(2)°, correspondingly.

Therefore, the short linkers exhibiting π-π and p-π conjugation, ferrocenyl and bispidinone moieties forms a rather strained and non-flexible macrocycle, which is partly relaxed by distorting one of the linkers.

It might be also noted that compound **6** exhibits only two intramolecular hydrogen bonds, forming 5-membered rings (Fig. 5, see Table S2 for details); no noticeable intermolecular interactions have been detected for the crystal.

This part of work shows that in all crystal structures the amide carbonyl groups attached to bispidine nitrogen atoms adopts the anti-conformation.

2.4. NMR studies

In $CDCl_3$ and DMSO solutions, acyclic compound **2** exist as a single anti-isomer because in the ^1H and ^{13}C NMR spectra two $C^{1,5}$ bridgehead atoms as well as two methyl groups each exhibit

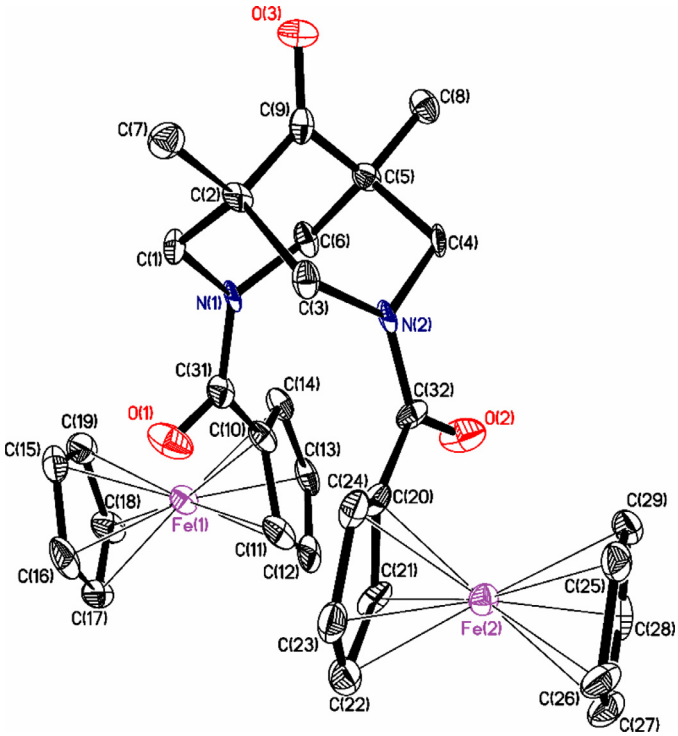
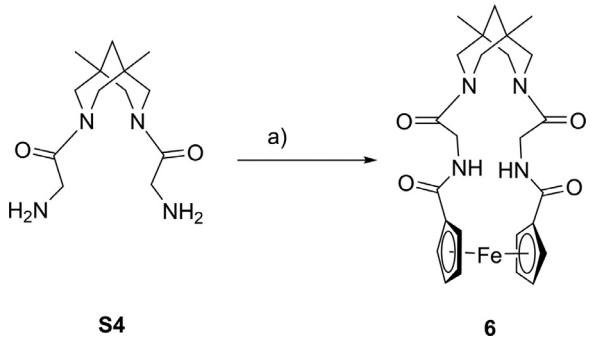


Fig. 2. Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 8. Cyclophane synthesis. (a) $Fc(COCl)_2$, DIPEA, DCM, 20°C. The synthesis of compound **S4** is described in SI.

a single peak, which indicates that they are chemically equivalent (C_2 axis of symmetry). At the same time, the signals of NCH_2 and $CH^{2',5'}$ ferrocene protons and carbons are strongly broadened at room temperature. We studied the dynamic behavior of **2** in $CDCl_3$ solution in the temperature range from 255 K to 323 K to estimate the rotation barrier of C-N amide bond (see SI). The slow exchange limit for ^1H and ^{13}C spectra is achieved at 255 K, the sets of narrow signals in both spectra strictly correspond to C_2 symmetry of anti-isomer. The barrier of amide rotation in **2** ($\Delta G^{\neq}$ = 60.8 ± 0.9 kJ/mol (14.5 ± 0.2 kcal/mol), (see SI) is in a good agreement with known values ($\Delta G^{\neq}$ = 13.4 – 15.4 kcal/mol) for 1,1'-ferrocene-bis-amides [42].

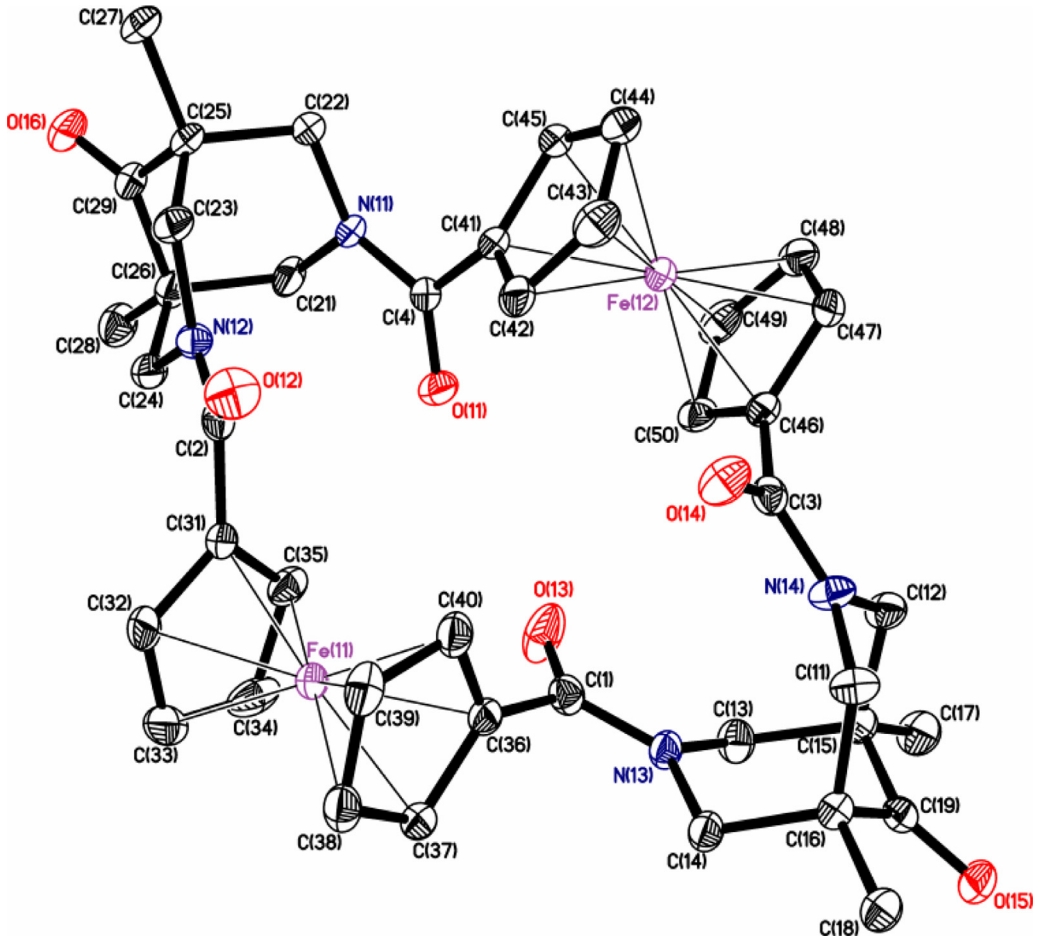


Fig. 3. Molecular structure of **5c²**. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

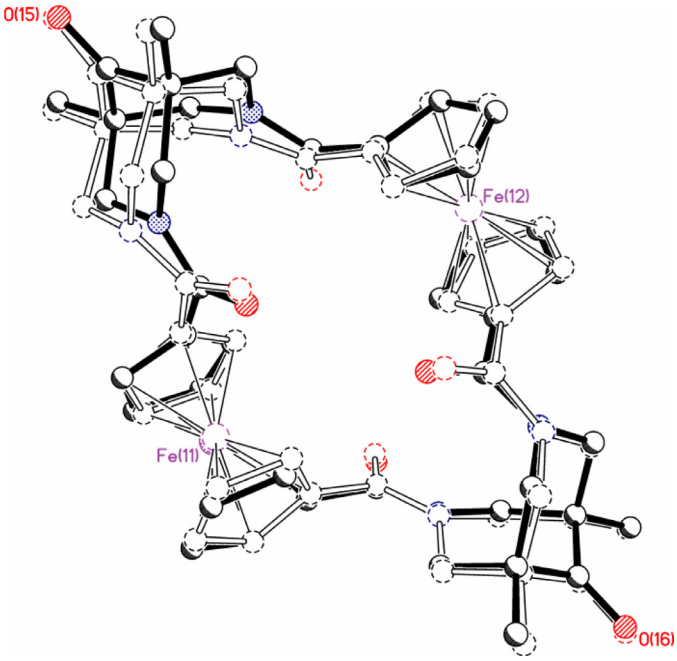


Fig. 4. Orthogonal fitting of two independent molecules in the structure **5c²**.

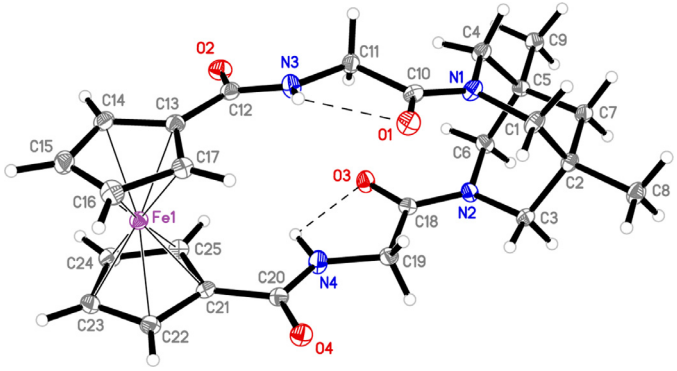


Fig. 5. Molecular structure of **6**. Thermal ellipsoids are shown at 50% probability level. NH…O hydrogen bonds are shown as dotted lines.

^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$ are consistent with its pseudo-C_{2v} symmetry (see Figs. S13 and S14). At ambient temperature the signals of protons and especialy carbon atoms of the piperazine cycle are markedlly broadened, which is likely due to chair-chair interconvertion.

NMR data for macrocycle **5c²** in both solvents are in excelent agreement with its X-ray diffraction structure (Figs. S15-S18). Its spectral patterns (with the exception of C_5H_5 singlets) at room temperature are similar to those of **2** at 255 K. The signals in DMSO-d_6 are somewhat broadened as compared to the solution in $CDCl_3$. (see Fig. S15 and Fig. S17) The spectral data unumbigously confirmed the presence of only anti-conformer in respect to mutual amide carbonyl group orientation.

NMR data for **6** are also consistent with its crystal structure (Fig. 5). The single signals of C 1,5 carbon atoms and methyl groups in both spectra are convincingly confirmed the anti-conformation of amide carbonyl groups at the bispidine framework. Therefore, from the NMR experiment we can conclude that the solution conformation for acyclic as well as cyclic compounds **2**, **5c²** and **6** is anti, so the rigid solid-state structures retains also in the solution.

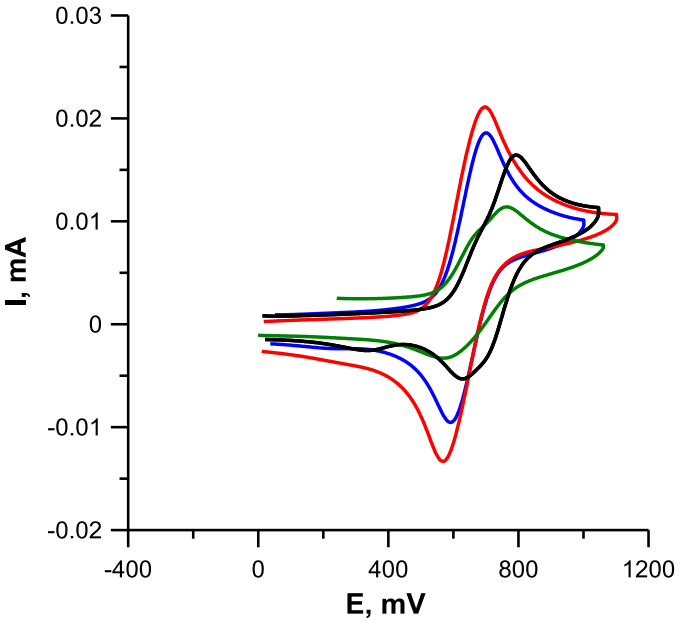


Fig. 6. CV curves of compounds **2** (red), **3** (blue), **5c²** (green) and **5c³** (black). DMF in presence 0.1 M Bu_4NClO_4 at a GC electrode; potential scan rate 100 mV s^{-1}.

2.5. Electrochemistry

Compounds **2**, **3**, **5c²** and **5c³** were investigated with cyclic voltammometry (CV) on rotating disk electrode, glassy carbon (GC) and gold electrodes. Redox properties slightly depended on materials of electrode. Electrochemical potentials were shown on Table S3 and CV curves on Fig. 6.

Investigated compounds didn't show any electrochemical activity in cathodic region (no reduction peaks were observed up to -2500 mV for all compounds). In anodic region, only peaks corresponding to oxidation of ferrocene fragments presented. As expected, electron-withdrawing amide groups shifted potentials of these peaks up to 140-170 mV as compared to unsubstituted ferrocene. It is interesting to note that in noncyclic compounds **2** and **3** both ferrocene fragments oxidized independently but simultaneously thus giving two-electron wave (Fig. 6). However, in cyclic **5c²** and **5c³** we observed splitting of oxidation peaks that can prove their sequential reduction. Probably, the first ferrocenium cation approximates to the second electron-donating non-oxidized iron atom that reduces its capability to oxidize. Of interest, this effect is stronger manifested in the case of trimeric molecule compared to the dimeric one.

3. Conclusion

In this work we have demonstrated that bispidine-ferrocene cyclophanes could be obtained using simple amidation reaction between 1,1'-bisferrocenoyl dichloride and bispidine-based diamines. Two new types of macrocycles have been designed, synthesized, isolated, and thoroughly studied. The X-ray and NMR have shown the predominance of anti-conformers for all compounds in the crystal state and in the solution. The further development of the BFC chemistry for the purposes of supramolecular sensing and catalysis is a subject of current study in our laboratories.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121945.

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