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Novel ferrocene-containing helical triangular macrocycle achieved *via* an exchange reaction

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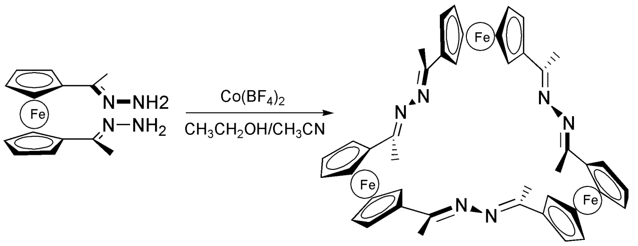
A novel ferrocene-containing helical triangular macrocyclic compound has been constructed through an exchange reaction of hydrazone groups which templated and catalyzed by Co(II) ions.

The design and study of various metal-containing macrocycles and cages is one of the most active and interesting areas in modern supramolecular chemistry.[1] A considerable variety of frequently predesigned molecular polygons and polyhedra have been established, and a methodology exists how to combine angular and linear building blocks to generate a particular ensemble.[2] In sharp contrast to the numerous examples of supramolecular architectures reported, the number of metal-containing molecular triangles is small,[3,4] mainly due to the impossibility of generating a 60° turning angle in a metal fragment of common coordination numbers. Virtually all the molecular triangles with metal entities at the corners display angles of 80–90°[5] and the flexibility of the organic ligand in essence enables formation of the triangle. In view of the previous work reported,[6] it is found that the conformational freedom of ferrocene afforded opportunities to generate various turning angles, due to a low-energy rotational barrier of the two Cp rings about the coordination axis. It seems that ferrocene moieties could be used as the corners of triangular macrocycle. Generally, ferrocene is treated as a common aromatic group, which made it unnecessary to construct metal–C coordination bonds in the creation of ferrocene-containing supramolecular architectures.[7] In this paper, we use 1,1′-diacetylferrocene dihydrazone as a starting material to synthesize a [3 + 3] analogous Schiff-base metal-containing macrocycle with ferrocene(diyl) fragments at corners through an easy exchange reaction of hydrazone groups in the presence of Co(II) ions (Scheme 1). To the best of our knowledge, only two ferrocene-containing molecular triangles have been documented in the literature.[3]

While two molecules of 1,1′-diacetylferrocene dihydrazone react to give the cyclic diazone [–N=(CH$_3$)C–C$_5$H$_4$FeC$_5$H$_4$–C(CH$_3$)=N–]$_2$ in the presence of Ba^{2+} or Mo^{2+} ions or hydrochloric acid,[8] treatment of 1,1′-diacetylferrocene dihydrazone with Co(BF$_4$)$_2$ in a 1 : 1 molar ratio in ethanol–acetonitrile solution leads to macrocyclic compound **1**† in high yield. Elemental analysis and spectroscopic characterization reveal the formation of a compound of the form [–N=(CH$_3$)C–C$_5$H$_4$FeC$_5$H$_4$–C(CH$_3$)=N–]$_n$. If Co(II) ions are absent, the exchange reaction of hydrazone can not occur even in the course of a month under the same conditions, although similar reactivity was used in the preparation of pure unsubstituted hydrazones in good yield by Newkome and Fishel.[9] In this case, it is reasonable to speculate that the Co(II) ions play a role as both template and catalyst in the course of the cyclocondensation reaction but then drops out from the resulting macrocycle in the solid state upon crystallization, a rare observation in the synthesis of macrocyclic compounds.



Scheme 1

The X-ray structure of macrocyclic compound **1**‡ (Fig. 1) shows the triangular macrocycle with the [C$_5$H$_4$C(CH$_3$)=N–N=C(CH$_3$)C$_5$H$_4$] conjugated units linking the three metal centers overlapping, in a progressive manner: in each unit, one cyclopentadienyl moiety lies above the averaged plane of the molecule, whilst the other cyclopentadienyl moiety lies below the averaged plane, forming a triangular cyclohelix. Since the triangle positions at the C_3 symmetry axis (2/3, 1/3, z), the three [C$_5$H$_4$C(CH$_3$)=N–N=C(CH$_3$)C$_5$H$_4$] units are equivalent with a metal–metal separation of *ca.* 9.13 Å. All the bond distances in the two arms are intermediate between the corresponding single bond and double bonds indicating extensive delocalization over the entire molecular skeleton. The skeleton ferrocenes are found to have ordinary Fe–C bond distances. In each ferrocene fragment of **1**, the torsion angle of the two arms is *ca.* 77°, which is favoured for most ferrocene derivatives in the crystal structures[10] and permit the formation of the triangular compound in this case. No significant deformation of the almost parallel cyclopentadienyl rings is observed for the ferrocene entities, and the dihedral angle between Cp rings in one [C$_5$H$_4$C(CH$_3$)=N–N=C(CH$_3$)C$_5$H$_4$] unit is *ca.* 80°. The outer diameter and height of the triangle are 13.5 and 4.1 Å, respectively. The shortest distance between the centroid and atoms in the macrocycle is *ca.* 3.3 Å, indicating that the size and shape of cavity at the center of the triangle are suitable for including a small guest but is unsuitable for Co(II) ion. Indeed, an acetontrile molecule is included in the cavity with a C(9)···N(1) separation of *ca.* 3.39 Å, and this acetonitrile

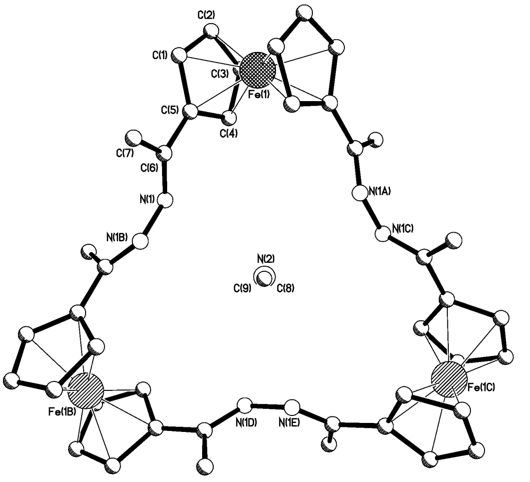


Fig. 1 Molecular structure of the helical triangular macrocycle with hydrogen atoms omitted for clarity. Symmetry code A: −2/3 + y, 2/3 + x, 1/6 − z; B: 4/3 + x − y, 4/3 − y, 1/6 − z, C: 2 − y, 2 + x − y, z; D: 4/3 − x, 2/3 − x + y, 1/6 − z; E: −x + y, 2 − x, z.

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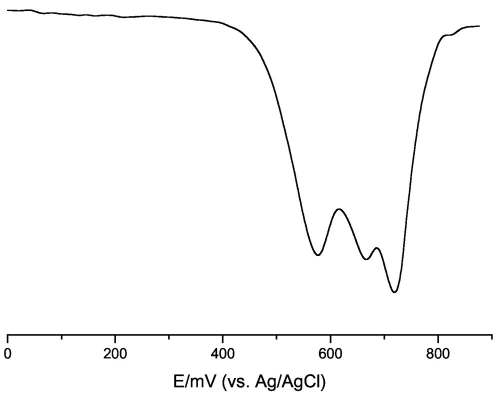

Fig. 2 Differential pulse voltammetry for compound **1** (1.0×10^{-4} M) in CH_2Cl_2 containing n-Bu_4NClO_4 (0.1 M), details of experimental conditions have been described in ref. 12.

molecule sites on a 3-fold axis position and is disordered into two half-occupancy positions.

Bridged biferrocenes have been proven to be good candidates for mixed-valence compounds.[6b,7,11] Differential pulse voltammetry of **1** (Fig. 2) shows three peaks with half-wave potentials ($E_{1/2}$) at 0.58, 0.66 and 0.72 V,[12] respectively, corresponding to the three single-electron oxidations of the ferrocene moieties. The ΔE values of *ca.* 0.08 and 0.06 V indicate a certain extent of interaction between the three ferrocene moieties.

In summary, this paper describes the construction of a triferrocene cyclohelical compound using a metal-directed exchange reaction. The incorporation of ferrocene units into macrocycles is of interest in the synthesis of new receptors containing redox-active groups and binding sites for the electrochemical recognition of cationic, anionic and neutral substrates.[13] The use of redox active ferrocene units as parts of the triangle may indeed lead to sensors based on electrochemical detection.[14]

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Notes and references

† *Synthesis of compound* **1**: to an ethanol solution (15 mL) of 1,1'-diacetylferrocene dihydrazone (0.075 g, 0.25 mmol) was added an acetonitrile solution (5 mL) of $Co(BF_4)_2$ (0.06 g, 0.25 mmol). The solution was stirred for 1 min and filtered. Then the resulting deep red solution was allowed to stand in air at room temperature for three days, yielding dark red crystals (0.06 g, 0.07 mmol) in a high yield (84%). The resulting sample was dried above P_2O_5 under vacuum. Anal. Calc. for $C_{44}H_{45}N_7Fe_3$: C, 63.0; H, 5.4; N, 11.7. Found: C, 63.3; H, 5.4; N, 11.5%. IR (KBr, cm^{-1}): ν = 3443.5m, 3089.3w, 2922.7m, 2291.8w, 2251.8w, 1600.3vs, 1470.5m, 1392.0m, 1357.7s, 1298.1m, 1284.8m, 1112.1m, 1035.3m, 1006.2m, 897.2m, 815.8m.

‡ *Crystal data* for **1**: $C_{44}H_{45}N_7Fe_3$, M_r = 839.42, hexagonal, space group $R\bar{3}c$, a = 13.590(2), c = 37.595(8) Å, V = 6013.1(17) Å^3, T = 293 K, Z = 6, μ(Mo-Kα) = 1.112 mm^{-1}, 22051 reflections measured, 1177 independent reflections (R_{int} = 0.121), R = 0.054, wR_2 = 0.161 for 842 observed reflections [$I > 2\sigma(I)$]. CCDC reference number 179470. See http://www.rsc.org/suppdata/cc/b2/b201459a/ for crystallographic data in CIF or other electronic format.

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12 The differential pulse voltammogram for the compound **1** was obtained in dichloromethane with n-Bu_4NClO_4 (0.1 M) as the electrolyte. A sweep rate of 25 mV s^{-1} was used in all pulse experiments. The cell comprises a platinum wire working electrode, a platinum auxiliary electrode and an Ag wire reference electrode. The ferrocene (1.0×10^{-3} M) was used as external standard with $E_{1/2}$ = 0.47 V *vs.* AgCl/Ag electrode.

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