Synthesis of a ferrocene bridged cyclam: a new redox-active macrocycle and the structure of a nickel(II) complex with strongly coupled metal centers

Herbert Plenio* and Clemens Aberle

Institut für Anorganische und Analytische Chemie, Albertstr. 21, 79104 Freiburg, Germany.
E-mail: plenio@uni-freiburg.de

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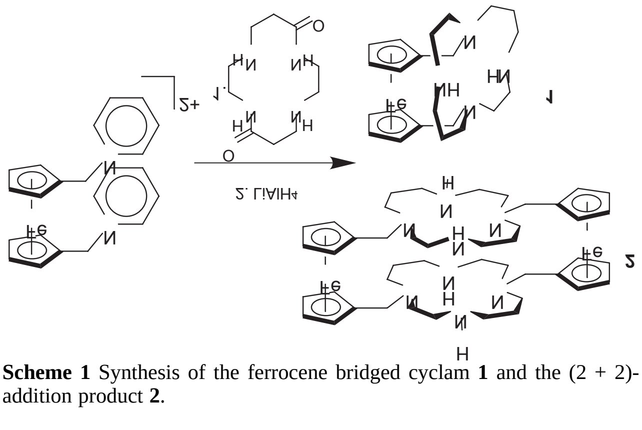
The reaction of 1,1′-ferrocene-bis(methylenepyridinium) with 1,4,8,11-tetraazacyclotetradecane-5,12-dione followed by reduction of the product with $LiAlH_4$ results in a ferrocene bridged cyclam, which is a very efficient redox-switch for transition metal ions due to the short iron-to-metal ion distances.

Cyclam (1,4,8,11-tetraazacyclotetradecane) and its numerous derivatives are among the most important macrocyclic ligands;[1] its coordination chemistry is well explored[2] and a number of cyclam–metal complexes are catalytically active.[3]

We were interested in synthesizing a ferrocene-bridged cyclam, since we anticipated that this would result in short distances between the ferrocene iron and any metal ion coordinated within the tetraaza-macrocycle. Consequently the interactions between the different metal centers are expected to be very strong and redox reactions at the ferrocene should have a pronounced effect on the properties of cyclam and those of the metal ions coordinated by it. This should add a new dimension to the coordination chemistry of cyclam and allow the design of new molecules for the electrochemical sensing of transition metal cations[4] and anions,[5] redox-switched catalysis,[6] the redox-switched bonding of metal ions[7] and biomimetic chemistry.[8]

However, partially substituted cyclams are less easily available and only recently a very convenient synthesis utilizing 1,4,8,11-tetraazacyclotetradecane-5,12-dione was presented by Guilard and coworkers.[9] In order to generate the ferrocene bridged cyclam, 1,1′-ferrocene-bis(methylenepyridinium) was reacted with 1,4,8,11-tetraazacyclotetradecane-5,12-dione in refluxing acetonitrile (Scheme 1).† After chromatographic work-up two main products were isolated: the 1 + 1-addition product (yield *ca*. 50%), the 2 + 2-addition product (yield *ca*. 24%) and a small amount of 3 + 3-product (*ca*. 5%). The total yields and the ratios of the different oligomers depended on the concentration of the reactants in the reaction mixture and it is possible to raise the amount of the 2 + 2- and 3 + 3-product significantly by decreasing the amount of solvent. Ferrocene-cyclam **1** can be synthesized in 86% yield from the initial 1 + 1-product by reduction with $LiAlH_4$. The 2 + 2-product can also be reduced in this manner resulting in the respective cofacial bis(ferrocene-cyclam) **2**.



Scheme 1 Synthesis of the ferrocene bridged cyclam **1** and the (2 + 2)-addition product **2**.

Initially we were interested in the electrochemical properties of the ferrocene-cyclam and its transition metal complexes. Table 1 lists redox data obtained by cyclic voltammetry in acetonitrile from which it is obvious that the magnitude of the redox shifts and hence the redox-switching effect per single metal ion is enormous, when for example compared to the $\Delta E_{1/2}$ values of related ferrocenyl-substituted cyclams[10,11] ($\Delta E_{1/2}$ < 100 mV) and is significantly larger than those of aminoferrocene metal complexes synthesized by us.[12]

To better understand the coordinating properties of **1** as well as the origin of the extremely large redox shifts we attempted to crystallize a metal complex of this ligand and were successful with $Ni(CF_3SO_3)_2$ (Fig. 1).‡ In the crystal, nickel is coordinated in the center of the tetraazamacrocycle in a square-planar environment, which is only slightly distorted, even though the oxygen atom of an acetone molecule displays a weak contact to Ni^{2+} [Ni1–O2 320.8(9) pm]. This square-planar geometry also appears to be present in solution as evidenced by the diamagnetic nature of the complex in acetonitrile. The stereo-

Table 1 Electrochemical data of **1** and transition metal complexes as determined by cyclic voltammetry in MeCN using NBu_4PF_6 as supporting electrolyte *vs*. cobaltocene ($E_{\frac{1}{2}}$ = −0.94 V) or ferrocene ($E_{\frac{1}{2}}$ = +0.40 V) reference

	$E_{\frac{1}{2}}$/V(Fe^{II}–Fe^{III})	$\Delta E_{\frac{1}{2}}$/mV
1	+0.33	—
1·$Co(CF_3SO_3)_2$	+0.69	+360
1·$Ni(CF_3SO_3)_2$	+0.71	+380
1·$Cu(CF_3SO_3)_2$	+0.74	+410
1·$Zn(CF_3SO_3)_2$	+0.80	+470

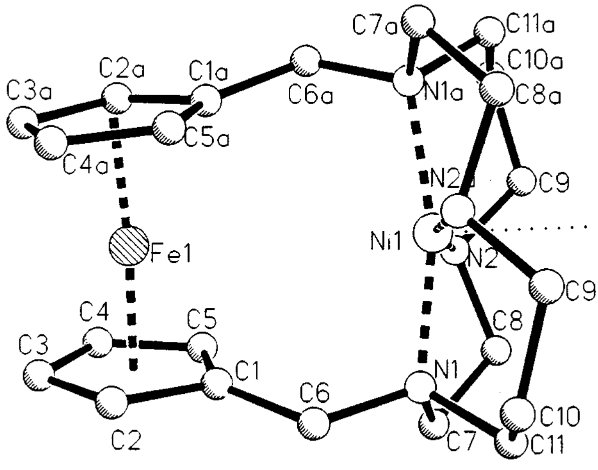


Fig. 1 Crystal structure of **1**·$Ni(CF_3SO_3)_2$ (acetone molecule, counter ions and hydrogen atoms omitted for clarity). Important bond lengths, interatomic distances (pm) and bond angles (°): Ni–N1 195.9(4), Ni–N2 194.8(5), Fe1–Ni1 385.4(8), N1–Ni–N1a 166.1(3), N2–Ni–N2a 162.4(3), N1–Ni–N2a 95.1(2), N1–Ni–N2 87.0(2).

chemistry of **1**·Ni(CF_3SO_3)$_2$ in the solid state is *trans*-I according to the Bosnich classification[13] and consequently both N–H vectors point approximately towards the ferrocene. Another unusual feature of this crystal structure is the rather short distance between iron and nickel [385.4(8) pm] and this can easily explain why upon Ni^{2+}-coordination the iron redox potentials are perturbed drastically. The above mentioned distance might be too long to account for a significant interaction (other than electrostatic) between the metals, but it once again raises the question about the possibility of bonding interactions between the iron in ferrocene and metal cations.[14] The fact that the ferrocene HOMO is predominantly localized on iron has nurtured speculation about donor–acceptor type interactions between the ferrocene iron and other metal ions. Investigations of metal ion complexes of ferrocene-cyclam **1** could provide a more conclusive answer to this question. The geometry of the ferrocene unit itself is essentially unremarkable though not ideal as evidenced by the small tilt (6.4°) of the respective planes of the two cyclopentadienyl rings; a more significant distortion is observed in the methylene groups (C6, C6a) which deviate from the respective cyclopentadienyl plane by 10.5°.

In conclusion this communication offers a simple two step synthesis of a redox-active cyclam ligand in which, owing to the intimate coupling of the metal centers, redox reactions at the ferrocene will strongly alter the coordination characteristics of the ligand.

Notes and references

† *Synthesis of ferrocene cyclam*. **A.** 1,1′-ferrocene-bis(methylenepyridinium) chloride tosylate (5.12 g, 9.02 mmol), 1,4,8,11-tetraazacyclotetradecane-5,12-dione (2.06 g, 9.02 mmol) and Na_2CO_3 (7.0 g) were added to acetonitrile (300 mL) and heated under reflux for 60 h. The cold reaction mixture was filtered and the filtrate evaporated to dryness. The residue was purified by chromatography ($CHCl_3$–MeOH = 10 : 1) to yield ferrocene–cyclamdione (2.0 g, 50%), 2 + 2-product (0.94 g, 24%) and 3 + 3-product (*ca*. 0.20 g, 5%). EIMS: 438 (M^+); ^1H NMR ($CDCl_3$) δ 2.11–2.29 (m, 6H), 2.58–3.36 (m, 10H), 3.82–4.08 (m, 12H), 8.97 (s, NH), 9.02 (s, NH). **B.** Ferrocene–cyclamdione (4.4 g, 10 mmol) was dissolved in a mixture of thf (100 mL) and $CHCl_3$ (200 mL). To the ice-cooled solution was added $LiAlH_4$ (7.6 g, 200 mmol) and stirring continued for 48 h. After careful hydrolysis of excess $LiAlH_4$ with water (70 mL), 15% aq. NaOH (200 mL) were added and the product extracted with $CHCl_3$. The organic layer was separated, dried over $MgSO_4$, filtered and the filtrate evaporated to dryness. The residue was purified by chromatography (MeOH–Et_2NH = 10 : 1) to yield 3.5 g (86%) of **1**. ^1H NMR ($CDCl_3$) δ 1.40 (d, 14 Hz, 2H), 1.85 (d, 12 Hz, 2H), 2.14 (d, 11 Hz, 4H), 2.46–2.95 (m, 14H), 3.22 (td, 7 Hz, 3 Hz, 2H), 3.73 (s, 2H), 3.93–4.08 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 25.64, 47.02, 51.55, 53.40, 53.49, 58.20, 65.37, 65.76, 67.40, 70.26, 88.35. All compounds have been characterized by elemental analysis and NMR spectroscopy.

‡ *Crystal data for* **1**: $C_{27}H_{40}F_6FeN_4NiO_7S_2$, M = 825.3, T = 293 K, tetragonal space group $P4_32_12$, $a = b$ = 10.5735(15), c = 30.251(6) Å, V = 3382.0(10) Å^3, Z = 4, D_c = 1.621 g cm^{-3}, F (000) = 1704, μ(Mo-Kα) = 1.19 mm^{-1}, θ-range: 2.7–25.97°, reflections (collected/unique): 3524, 3137, refinement: full matrix least squares on F^2, data–parameters: 3137/219, final R-indices [$I > 2\sigma(I)$]: $R1$ = 0.0452, $wR2$ = 0.110, largest diff. peak and hole: +0.419, −0.370 e Å^{-3}. The structure was solved and refined using the SHELX-97 program suite.[15] CCDC 182/1077. See http://www.rsc.org/suppdata/cc/1998/2697 for crystallographic files in .cif format.

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