Host Molecules containing Electroactive Cavities obtained by the Molecular Assembly of Redox-active Ligands and Metal Ions

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Self-assembly processes of nickel ions with the redox-active ligand 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane (Fc$_4$cyclam) induces the formation of a redox-active cavity of potential use in electrocatalysis.

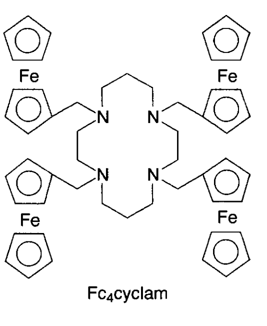
Among systems which could be capable of acting as mediators in redox reactions are ferrocene derivatives which are known to display reversible one-electron oxidation processes at modest anodic potentials. An important challenge in this field is the design and synthesis of redox mediators[1,2] which could transfer several electrons simultaneously at the same potential in order to avoid high-energy pathways which are usually involved in single-electron processes.[2] It has recently been observed [3,4] that the occurrence of a metal ion (Lewis acid) and multiple redox-active units in transition metal complexes bearing electroactive groups makes them good candidates as redox-catalytic systems capable of promoting redox reactions on a guest substrate through a combination of guest inclusion and subsequent Lewis acid catalytic activation.

Towards this goal we have prepared transition metal complexes of a ligand bearing electroactive groups, 1,4,8,11-tetra(ferrocenylmethyl)-1,4,8,11-tetraazacyclotetradecane (Fc$_4$cyclam), following literature procedures by the reaction of cyclam with (ferrocenylmethyl)trimethylammonium iodide.[4] We have found that the use of different metal ions appears to control the assembly of the electroactive Fc$_4$cyclam molecule into a different conformation, leading in some instances to the synthesis of metals containing an electroactive cavity surrounding the metal–substrate framework.

Reaction of Fc$_4$cyclam with Cu(O$_2$CMe)$_2$·H$_2$O in methanol allowed the isolation, by slow evaporation of the solvent, of small crystals of [Cu(Fc$_4$cyclam)][ClO$_4$]$_2$.† A view of the molecule is shown in Fig. 1 with the atomic numbering scheme. Copper is coordinated by four coplanar nitrogen atoms from the ligand. Two axial Cu–O distances were found: Cu(1)–O(8) = 2.537(8) and Cu(1)–O(4) = 3.257(8) (only the shortest Cu–O distance is included in Fig. 1). The Fc$_4$cyclam ligand shows the more thermodynamically favourable isomer with the two ferrocenylmethyl groups above the N$_4$ plane and the remaining two below the N$_4$ plane.[5] The reaction of Fc$_4$cyclam with Ni(O$_2$CMe)$_2$·4H$_2$O in refluxing methanol and the further addition of [NH$_4$][PF$_6$] allowed the isolation of a solid which was crystallised by slow diffusion of diethyl ether into acetonitrile solutions of the complex, yielding yellow–green crystals which were formulated as [Ni(Fc$_4$cyclam)(MeCN)][PF$_6$]$_2$·2MeCN.‡ Out of the mother liquor the crystals were unstable owing to loss of solvent.

Low-temperature single-crystal X-ray procedures were used to determine the molecular structure of the nickel(II) complex. The structure consists of [Ni(Fc$_4$cyclam)(MeCN)]$^{2+}$ units and hexafluorophosphate anions linked by ionic interactions. Two molecules of acetonitrile complete the molecular packing. A view of the cation with the atomic numbering scheme is depicted in Fig. 2(*a*). The four nitrogen atoms from the macrocycle are not planar with out-of-plane deviations of 0.26 Å. The coordination geometry about the nickel(II) atom is between square pyramidal and trigonal bipyrimidal. In contrast with the copper(II) complex, the ligand shows a conformation with the four ferrocenylmethyl groups pointing above the N$_4$ plane. A similar conformation has been found in, for example the nickel(II) complex containing [Ni(Me$_4$cyclam)]$^{2+}$, Me$_4$-cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetra- azacyclotetradecane.[6] The consequence of coordination of nickel with Fc$_4$-cyclam determines the formation of a host molecule containing an electroactive cavity built with the four ferrocenyl groups. To our knowledge this is the first time that a crystallographic characterisation fo a metal complex containing an electroactive cavity has been published. Fig. 2(*b*) shows two space-filling representations of the structure emphasizing the metal substrate (MeCN) association surrounded by ferrocenyl groups.

The electrochemical behaviour of Fc$_4$cyclam and the corresponding metal ions have been investigated by cyclic voltammetry, rotating disk electrode and coulometry. Electrochemical experiments were carried out at room temperature in the presence of [Bu$^n{}_4$N][PF$_6$] as supporting electrolyte and using as solvent a mixture of CH$_2$Cl$_2$–MeOH (1 : 1 *v*/*v*) in order to dissolve both Fc$_4$cyclam and the metal ions. The free ligand shows a unique oxidation wave at $E_{1/2}$ = 0.385 V *vs.* SCE. By



Fc$_4$cyclam

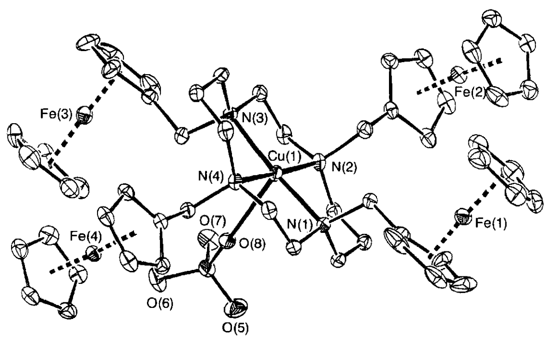


Fig. 1 Molecular structure of the cation [Cu(Fc$_4$cyclam)]$^{2+}$ showing the atomic numbering scheme. Selected bond lengths (Å) and angles (°): Cu(1)–N(2) 2.068(8), Cu(1)–N(1) 2.081(7), Cu(1)–N(3) 2.082(7), Cu(1)–N(4) 2.090(8), Cu(1)–O(8) 2.537(8); N(2)–Cu(1)–N(1) 93.0(3), N(2)–Cu(1)–N(3) 87.0(3), N(1)–Cu(1)–N(3) 176.3(3), N(2)–Cu(1)–N(4) 176.0(3), N(1)–Cu(1)–N(4) 85.9(3), N(3)–Cu(1)–N(4) 93.8(3), N(2)–Cu(1)–O(8) 91.9(3), N(1)–Cu(1)–O(8) 90.0(3), N(3)–Cu(1)–O(8) 93.7(3), N(4)–Cu(1)–O(8) 91.9(3).

addition of copper the solution turns blue and a displacement of the half-wave potential to more anodic potentials ($E_{1/2}$ = 0.479 V; $\Delta E_{1/2}$ = 94 mV) was observed. A similar $E_{1/2}$ value was found when the complex $[Cu(Fc_4cyclam)][ClO_4]_2$ was electrochemically studied under the same conditions. The complex shows an additional reduction wave at $E_{1/2} = -0.142$ V which is attributed to the reduction of the copper(II) central atom. However, addition of $Ni(O_2CMe)_2{\cdot}4H_2O$ to a solution of the ligand does not affect the redox potential of the ferrocenyl groups. This contrasts with the fact that if the isolated complex $[Ni(Fc_4cyclam)(MeCN)][PF_6]_2$ obtained in refluxing methanol is electrochemically studied under the same conditions a ferrocenyl oxidation potential shift ($\Delta E_{1/2}$ = 64 mV) is clearly observed when compared with that of Fc_4cyclam. The behaviour observed for nickel may be explained assuming that the $[Ni(Fc_4cyclam)]^{2+}$ cation present in $[Ni(Fc_4cyclam)(MeCN)][PF_6]_2$ is not formed at room temperature under the working conditions, probably because of a slow complex-formation kinetic process (no shift in the oxidation potential was observed even after several days). That suggest that, from an electrochemical recognition viewpoint, slow complex-formation kinetics in redox-active ligands may be used to mask or enhance the presence of charged substrates such as nickel and copper, respectively, which were expected to display a similar effect on the oxidation potential of the ferrocenyl groups. In fact, we have found that the ligand Fc_4cyclam can selectively recognize copper in the presence of nickel. On the other hand, no well-defined processes were found for the oxidation or reduction of the nickel(II) complex within the solvent window. By controlled potential electrolysis at the ferrocenyl oxidation peak and coulometry for the Fc_4cyclam and the parent metal complexes, the final oxidation process was found after the passage of 4 F mol^{-1}, indicating that the compounds are four-electron reservoir complexes.

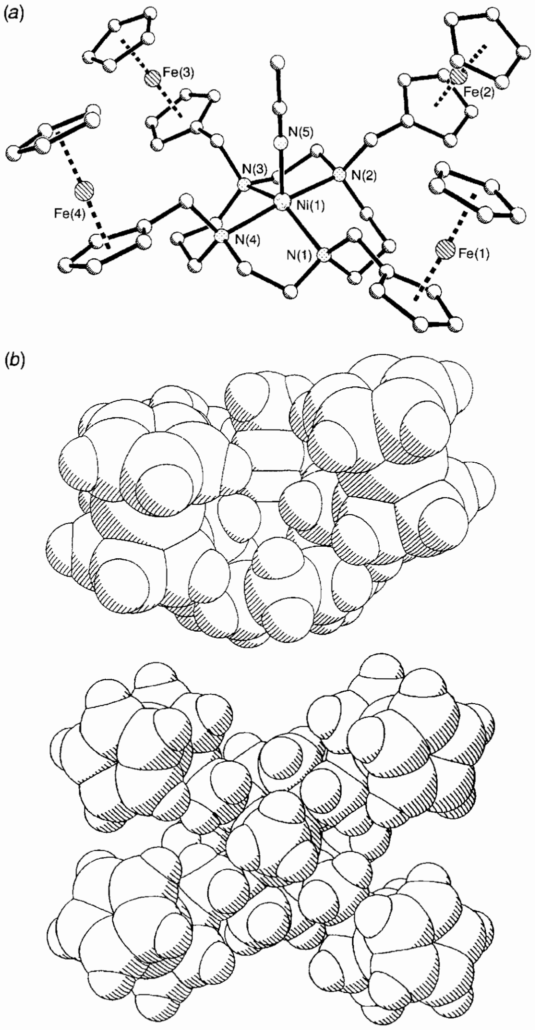


Fig. 2 (*a*) Molecular structure of the cation $[Ni(Fc_4cyclam)(MeCN)]^{2+}$ showing the atomic numbering scheme. (*b*) Two alternative space-filling representations emphasizing the host–guest association and the electro-active cavity. Selected bond lengths (Å) and angles (°): Ni(1)–N(1) 2.122(6), Ni(1)–N(2) 2.185(6), Ni(1)–N(3) 2.109(6), Ni(1)–N(4) 2.192(6), Ni(1)–N(5) 1.999(8); N(5)–Ni(1)–N(3) 106.4(3), N(5)–Ni(1)–N(1) 107.1(3), N(3)–Ni(1)–N(1) 146.5(3), N(5)–Ni(1)–N(2) 92.6(3), N(3)–Ni(1)–N(2) 84.6(2), N(1)–Ni(1)–N(2) 93.4(2), N(5)–Ni(1)–N(4) 91.8(3), N(3)–Ni(1)–N(4) 94.9(3), N(1)–Ni(1)–N(4) 84.5(3), N(2)–Ni(1)–N(4) 175.5(2).

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Footnotes

† *Crystal data* for $C_{54}H_{64}N_4Fe_4CuCl_2O_8$, M = 1254.93, monoclinic, space group $P2_1/c$, a = 17.721(8), b = 14.159(8), c = 22.741(15) Å, β = 110.44(5)°, Z = 4, U = 5347(8) $Å^3$, D_c = 1.55 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, T = 293(2) K, μ(Mo-Kα) = 16.1 cm^{-1}. A well-shaped crystal with approximate dimensions 0.1 × 0.05 × 0.1 mm was mounted on a Rigaku AFC7 diffractometer coupled to an Mo target rotating anode X-ray source. A total of 9752 reflections were recorded on a R-axis II imaging plate of which 6452 were unique (R_{int} = 0.051; $5 \leqslant 2\theta \leqslant 50°$). Lorentz and polarization corrections were applied but no allowance was made for absorption. The structure was solved by direct methods (SHELXTL PLUS)[7] and refined by full-matrix least-squares analysis on F^2 (SHELX-93).[8] The refinement converged at $R1$ = 0.0594 [$F > 4\sigma(F)$] and $R2$ = 0.1628 (all data). Largest peak and hole in the final difference map +0.77, −0.41 $eÅ^{-3}$.

‡ *Crystal data* for $C_{60}H_{73}N_7Fe_4NiP_2F_{12}$, M = 1464.28, monoclinic, space group $P2_1/c$, a = 10.896(2), b = 22.370(4), c = 25.331(5) Å, β = 96.39(3)°, Z = 4, U = 6136(2) $Å^3$, D_c = 1.563 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, T = 153(2) K, μ(Mo-Kα) = 13.6 cm^{-1}. A well-shaped crystal with approximate dimensions 0.21 × 0.19 × 0.14 mm was mounted on a Rigaku AFC7 four-circle diffractometer coupled to an Mo target rotating anode X-ray source. Intensity data were collected using low-temperature procedures. Unit cell dimensions were determined from the angular setting of 25 reflections. A monoclinic cell was obtained and the space group $P2_1/c$ was confirmed from the structure determination. A total of 8059 reflections were measured of which 7869 were unique (R_{int} = 0.027, $7.2 \leqslant 2\theta \leqslant 45.0°$) using the $2\theta/\omega$ method. The intensity of three standard reflections monitored every 60 min showed no systematic variation. Lorentz and polarization corrections were applied but no allowance was made for absorption. The structure was solved by direct methods (SHELXTL PLUS)[7] and refined by full-matrix least-squares analysis on F^2 (SHELX-93).[8] The refinement converged at $R1$ = 0.067 [$F > 4\sigma(F)$] and $R2$ = 0.253 (all data). Largest peak and hole in the final difference map +2.50, −1.58 $eÅ^{-3}$.

Atomic coordinates, bond lengths and angles, and thermal parameters for both complexes have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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