Redox-Driven Intramolecular Anion Translocation between Transition Metal Centres

Luigi Fabbrizzi,* Francesco Gatti, Piersandro Pallavicini, and Eugenia Zambarbieri[a]

Abstract: In a two-component system containing two transition metal centres, M_1 and M_2, an anion X^- coordinated to M_1 can be translocated to M_2, if i) the latter metal is redox active (through the $M_2^{n+}/M_2^{(n+1)+}$ change) and ii) the affinity towards X^- decreases along the series: $M_2^{(n+1)+} > M_1 > M_2^{n+}$. In these circumstances, when the $M_1 \sim M_2$ system is in its reduced form, X^- stays on M_1; on oxidation X^- moves to M_2. The above-mentioned model has been verified with the covalently linked two-component system **1**, in which a tripodal tetramine subunit (tren) hosts a Cu^{II} ion, and a tetramine macrocyclic subunit (cyclam) encircles a nickel centre, which is redox active through the Ni^{II}/Ni^{III} couple. Binding tendencies of inorganic anions towards the Cu^{II}, Ni^{II} and Ni^{III} ions, in an MeCN solution, were investigated and compared with those involving the separate components $[Cu^{II}(\mathbf{2})]^{2+}$ and $[Ni^{II,III}(\mathbf{3})]^{2+/3+}$. In general, affinity towards X^- decreases along the series: $Ni^{III} > Cu^{II} > Ni^{II}$. Thus, we observed through spectroelectrochemical techniques that in the reduced form of the two-component system $Cu^{II} \sim Ni^{II}$, the X^- anion (Cl^-, NCO^-) is located on the Cu^{II} centre, whereas on Ni^{II}-to-Ni^{III} oxidation it is translocated to the Ni^{III} centre. The translocation is quickly reversible and, in the case of the oxidation resistant chloride anion, can be carried out indefinitely through consecutive oxidation and reduction processes, in a controlled potential electrolysis experiment. The intramolecular nature of the redox-driven anion translocation in the $Cu^{II} \sim Ni^{II,III}$ system is discussed and substantiated by considering the pertinent thermodynamic functions ΔH^o and ΔS^o, obtained by temperature dependent voltammetric studies. We conclude that the intramolecular Cl^- translocation from Cu^{II} to Ni^{III} prevails over any other intermolecular process, due a more favourable entropy contribution.

Keywords: electrochemistry · ion translocation · macrocyclic ligands · molecular devices · tripodal ligands

Introduction

The control of movements at a molecular level represents one of the most appealing and challenging tasks of today's chemistry.[1] Typically, in a multicomponent system, either of supramolecular or molecular nature, one of the components can be moved with respect to the other(s) following an external stimulus (a pH change, the variation of the redox potential, a photonic input). Recent examples include: i) the shuttling of a π-acceptor molecular wheel between the two π-donor stations of the axis in a rotaxane, controlled through either a redox or an acid–base reaction,[2] ii) the electrochemically triggered half-turns of a coordinating ring in a copper (2)-catenate,[3] and iii) the pH-driven swinging of a fluorescent side chain in a Ni^{II} scorpionate complex.[4] All the above mentioned systems convert energy into mechanical work and can be considered as machines that operate at a molecular level.[5] The movement generates (and is perceived by) the drastic change of a given property (e.g. the colour, the luminescent emission), which is said to be switched ON or OFF. The switch metaphor is further accounted for by the fact that the activation of the property follows a mechanical event, in analogy with the behaviour of the everyday life switches, which typically turn the light of a bulb ON or OFF, when operated by a finger.

Other ways exist to carry out mechanical work at a molecular level: one involves the intramolecular translocation of an ionic particle from a given site to another of the same molecular system. For instance, iron can be intramolecularly relocated into two defined positions of a ditopic receptor containing both a tris-hydroxamate component (a hard environment, suitable for Fe^{III} coordination) and a tris-2,2′-bipyridine component (a soft environment, suitable for low-spin Fe^{II} coordination).[6] Thus, changing of the oxidation state, through chemical reduction (with ascorbic acid) and oxidation (with peroxydisulphate), makes the metal move from the hard component to the soft one, and vice versa. The redox-driven translocation is sluggish, taking place in minutes and hours, probably due to the serious conformational changes the ditopic system has to undergo in order to accommodate the metal centre of the given oxidation state in its preferred location.

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Also anions can be translocated from a site to another within a molecular system, taking profit from a redox-potential gradient. The anion-binding sites can be two metal centres, M_1 and M_2, hosted by a ditopic receptor. In particular, one of the two metal centres should be able to attain two consecutive oxidation states of comparable stability, each one displaying a distinctly different affinity toward the anion. We have recently reported the electrochemically driven anion translocation between metal centres in a supramolecular coordination compound (i.e., a system in which the different components, metal complexes, were held together by non-covalent interactions).[7] We describe here a system in which the two metal-hosting subunits are firmly linked by covalent bonds. One of the subunits, a tripodal tetramine, hosts the Cu^{II} ion to which it imposes a trigonal bipyramidal stereochemical arrangement, whose vacant axial position is available for anion binding. The other subunit, a tetramine ring, hosts a nickel centre and promotes the fast and reversible redox change between two oxidation states displaying a strikingly different affinity towards anions: high for Ni^{III}, low or nil for Ni^{II}. The described ditopic receptor represents an ideal model for the reversible intramolecular anion translocation between metal centres driven by a redox-potential gradient, whose thermodynamic basis can be stated and verified.

Results and Discussion

The design of the ditopic receptor for the redox-driven translocation of an anion X^- between two metal centres M_1 and M_2: An X^- anion can be moved between two metal centres M_1 and M_2 hosted by the same molecular (or supramolecular) system, following an electrochemical input. One of the two metal ions, for example M_2, must be able to exist in two oxidation states of comparable stability, M_2^{n+} and $M_2^{(n+1)+}$, linked by a fast and reversible one-electron redox change.

When M_2 is in its reduced form M_2^{n+}, X^- stays on the M_1 centre; when M_2^{n+} is oxidised to $M_2^{(n+1)+}$, X^- prefers to stay on M_2. Thus the M_2^{n+}-to-$M_2^{(n+1)+}$ change induces the translocation of X^- from M_1 to M_2; on the other hand, on $M_2^{(n+1)+}$-to-M_2^{n+} reduction, X^- goes back to the M_1 station. This behaviour requires that the three states display very different binding tendencies towards X^-: in particular, the affinity should decrease according to the sequence: $M_2^{(n+1)+} \gg M_1 \gg M_2^{n+}$. Such a situation is illustrated in the square scheme reported in Figure 1.

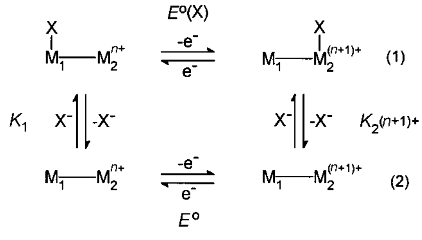


Figure 1. The square scheme illustrating the thermodynamic bases of the translocation of an X^- anion from the metal centre M_1 to the metal centre M_2, following the M_2^{n+}-to-$M_2^{(n+1)+}$ oxidation process [equilibrium in Equation (1) in the Figure]. On $M_2^{(n+1)+}$-to-M_2^{n+} reduction, X^- moves back on M_1.

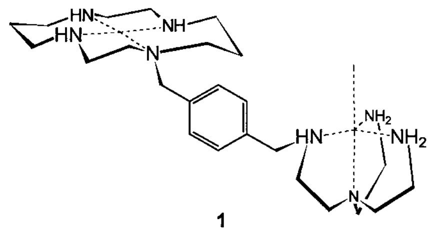
In particular, the redox-driven anion-translocation process is described by the horizontal equilibrium in Equation (1) in Figure 1, whose free energy change, $\Delta G^o_{trans(X)}$, is given by Equation (3).

$$\Delta G^o_{trans(X)} = -FE^o(X) \tag{3}$$

$$\Delta G^o_{trans(X)} = -FE^o(X) = -FE^o + RT\ln K_1 - RT\ln K_2^{(n+1)+} \tag{4}$$

F is the Farady constant, and $E^o(X)$ is the electrode potential associated with the $M_2^{(n+1)+}/M_2^{n+}$ couple in the $M_1 \sim M_2$ system, in presence of X^-. K_1 and $K_2^{(n+1)+}$ are the binding constants of X^- to M_1 and $M_2^{(n+1)+}$, respectively. Let us consider the case that $K_2^{(n+1)+}$ is much greater than K_1, which, in turn, is much greater than K_2^{n+} (i.e. the binding constant of X^- to M^{n+}, which in the present case, for sake of simplicity, is assumed to be nil). This leads to Equation (4), in which E^o is the electrode potential associated with the $M_2^{(n+1)+}/M_2^{n+}$ couple in the $M_1 \sim M_2$ system, in absence of X^- (the horizontal equilibrium [Eq. (2)] in the square Scheme of Figure 1). As $K_2 \ll K_2^{(n+1)+}$, we can derive from Equation (3) that $E^o(X)$ must be distinctly lower than E^o, that is, the addition of X^- to a solution containing the $M_1 \sim M_2$ ditopic system should cause a decrease of the $M_2^{(n+1)+}/M_2^{n+}$ redox potential. This is the most simple, yet efficient guideline to be observed when designing a dimetallic system suitable for redox-driven anion-translocation experiments.

The hosting framework chosen in the present work, **1**, consists of a tripodal tetramine subunit (tren) and of a tetramine macrocyclic ring (cyclam) covalently linked by an 1,4-xylyl spacer. The quadridentate tren ligand imposes trigonal bipyramidal geometry on the metal, thus leaving an axial position of the coordination polyhedron available for the coordination of an X^- anion. On the other hand, when encircled by cyclam, a metal centre may have two vacant sites, above and below the N_4 plane, and may give rise to a *trans*-octahedral coordinative arrangement.[9] Moreover, cyclam typically promotes the redox activity of the encompassed metal centre, generating a couple of consecutive oxidation states of comparable stability.[10]



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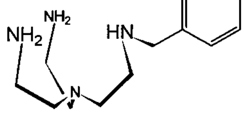
Copper(II), as M_1, and the nickel(II, III) couple, as $M_2^{(n+1)+}/M_2^{n+}$, fit the square scheme of Figure 1 well. In fact, Cu^{II} forms a stable complex with tren, and the $[Cu^{II}(tren)]^{2+}$ species forms a rather stable 1:1 adduct, $[Cu^{II}(tren)X]^+$, with inorganic anions in solution.[11] The $[Cu^{II}(tren)X]^+$ ion displays a trigonal bipyramidal geometry, ascertained through X-ray diffraction studies (X = Cl,[12] NCO,[12] NCS[13]). On the other hand, Ni^{II} is firmly encircled by the cyclam ring and undergoes reversible oxidation to Ni^{III} at a moderately positive potential.

Most importantly, $[Ni^{II}(cyclam)]^{2+}$ tends assume a square planar geometry (as a d^8 low-spin cation) and, when dissolved in polar solvents, it does not tend to bind further ligands in the two axial positions, so as to give a high-spin species.[14] In contrast, Ni^{III} (d^7, low-spin) strongly prefers a coordination number higher than 4 and binds two additional ligands in the axial positions, to give a *trans*-octahedral species.[15] Such a stereochemical arrangement has been ascertained in crystalline complexes, for example $[Ni^{III}(cyclam)Cl_2]ClO_4$, in which the two chloride ions occupy the axial positions of an elongated octahedron.[16]

The $[Cu^{II}Ni^{II}(\mathbf{1})]^{4+}$ dimetallic complex, indicated in the following as $Cu^{II} \sim Ni^{II}$, was prepared in two steps: i) The ditopic host **1** was first treated with one equivalent of Ni^{II}, in ethanol, at 70 °C: on mixing, the metal centre sought the cyclam ring, as $[Ni^{II}(cyclam)]^{2+}$ is a more stable complex than $[Ni^{II}(tren)]^{2+}$; this is a result of a) the enhanced stability of metal complexes with preoriented ligands (the *thermodynamic* macrocyclic effect) and b) to the strong preference of a d^8 cation for square-planar coordination. ii) Then, one equivalent of Cu^{II} was added, at room temperature, to the solution containing the $[Ni^{II}(\mathbf{1})]^{2+}$ monometallic species (not isolated). Notice that Cu^{II} would compete successfully for the tetramine ring with Ni^{II}, but that metal replacement is prevented from the inertness of the Ni^{II}-cyclam subunit (the *kinetic* macrocyclic effect). Thus, the Cu^{II} ion is satisfied with the coordination by the tren subunit of **1**. The $Cu^{II} \sim Ni^{II}$ complex was isolated as a pure compound and characterised through elemental analysis and ESI mass spectroscopy. Its UV/visible spectrum in an MeCN solution shows the absorption band of the Cu^{II}-tren subunit (band centred at 700 nm, $\varepsilon = 120\,\text{M}^{-1}\,\text{cm}^{-1}$); the band of the low-spin Ni^{II}-cyclam subunit is observed as a shoulder at 450 nm (obscured by the intense charge-transfer band of the Cu^{II}-tren fragment).

The solution behaviour of the separate components: For comparative purposes, we have investigated the behaviour in an MeCN solution of the separated components, which ideally constitute the dimetallic system $Cu^{II} \sim Ni^{II}$. However, we did not consider the Cu^{II} complex of plain tren and the Ni^{II} complex of plain cyclam, but those of the corresponding *N*-benzyl substituted derivatives **2** and **3**.



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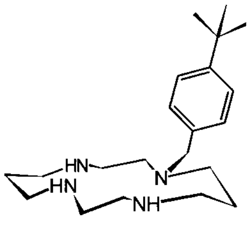

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The benzyl group mimics the spacer present in the ditopic receptor **1**. In fact, N-substitution is known to modify to an appreciable extent the coordinating tendencies of a polyamine. The $[Cu^{II}(\mathbf{2})](ClO_4)_2$ complex salt, when dissolved in MeCN, gives a blue solution, whose spectrum presents a broad band centred at 690 nm ($\varepsilon = 90\,\text{M}^{-1}\,\text{cm}^{-1}$). This spectral feature is typically observed with five-coordinate Cu^{II} polyamine complexes, displaying a trigonal bipyramidal stereochemistry.[8] Due to the very poor donating tendencies of the ClO_4^- ion, the vacant axial position should be occupied by an MeCN molecule. Addition of a coordinating anion like Cl^- induces a colour change from blue to green: in particular, an intense band develops at 470 nm (a Cl-to-Cu^{II} charge transfer), while the intensity of the d–d band at 690 nm and its maximum shifts to higher wavelengths.

Figure 2 displays the family of spectra obtained during the titration of $[Cu^{II}(\mathbf{2})]^{2+}$ with Cl^-. The plot of the molar absorbance versus chloride equivalents (Figure 2, inset), is consistent with the formation of a 1:1 adduct, $[Cu^{II}(\mathbf{2})Cl]^+$. Nonlinear least-squares analysis of the titration profile gave a $\log K$ value for the $[Cu^{II}(\mathbf{2})]^{2+} + Cl^- \rightleftharpoons [Cu^{II}(\mathbf{2})Cl]^+$ equilibrium of 5.73 ± 0.04. The NCO^- anion binds $[Cu^{II}(\mathbf{2})]^{2+}$ too, but with a lower affinity ($\log K = 5.0 \pm 0.1$). HSO_4^- and NO_3^- modify the $[Cu^{II}(\mathbf{2})]^{2+}$ spectrum only if added in large excess; the absorbance verus X^- equivalents profile indicates a binding constant K lower than 100.

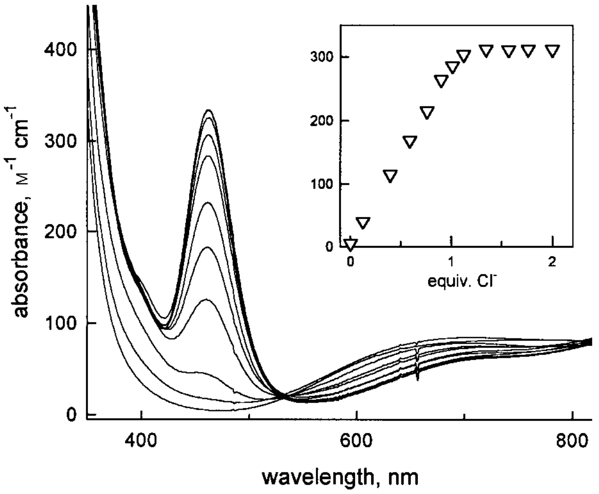


Figure 2. Spectrophotometric titration of an MeCN solution of $[Cu^{II}(\mathbf{2})]^{2+}$ with $[Bu_3Bz]Cl$. The increasing band at 470 nm corresponds to the formation of $[Cu^{II}(\mathbf{2})Cl]^+$. Inset: plot of the molar absorbance at 470 nm vs the equivalents of Cl^-. Least-squares analysis of the abs vs. equiv. profile gives a $\log K = 5.73 \pm 0.04$ for the equilibrium: $[Cu^{II}(\mathbf{2})]^{2+} + Cl^- \rightleftharpoons [Cu^{II}(\mathbf{2})Cl]^+$.

On the other hand, the $[Ni^{II}(\mathbf{3})]^{2+}$ complex in MeCN solution displays an absorption band centred at 470 nm, which is typical of a square-planar complex (d^8, low-spin, yellow in colour). The spectrum can be modified only on addition of an excess of a strongly coordinating anion (e.g., Cl^-). In particular, the intensity of the band at 470 nm decreases, while new weak bands are observed at 620 and 350 nm (shoulder). These bands refer to the high-spin octahedral species, in which one or two Cl^- anions are axially bound to the Ni^{II} centre. However, $[Ni^{II}(\mathbf{3})]^{2+}$ cannot compete with $[Cu^{II}(\mathbf{2})]^{2+}$ for the Cl^- anion. This is demonstrated by the fact that the titration with Cl^- of an MeCN solution containing equimolar amounts of $[Cu^{II}(\mathbf{2})]^{2+}$ and of $[Ni^{II}(\mathbf{3})]^{2+}$ produces a profile exactly superimposing on that reported in the inset of Figure 2, which had been obtained in absence of $[Ni^{II}(\mathbf{3})]^{2+}$.

Anion binding to the Ni^{III} centre can be easily followed by voltammetric studies with a platinum microsphere as a working electrode. In particular, the $[Ni^{II}(\mathbf{3})](ClO_4)_2$ complex salt, dissolved in an MeCN solution made 0.1 M in Bu_4NClO_4, undergoes a one-electron oxidation to Ni^{III}, at $E_{1/2} = 0.74$ V vs. Fc^+/Fc, as shown by the reversible cyclic voltammetry wave and by the symmetric differential pulse voltammetry (DPV) peak. It should be noticed that the $E_{1/2}$ value is more positive than that observed for the corresponding complex of plain cyclam, under the same conditions (0.60 V vs. Fc^+/Fc). The higher potential indicates that the Ni^{II}-to-Ni^{III} oxidation process is more difficult, probably due to the steric repulsion exerted by the bulky substituent towards the MeCN molecule(s) going to occupy the axial site(s). A similar behaviour had been previously observed for a series of nickel complexes with *N*-alkyl substituted fourteen-membered tetraaza macrocycles.[17]

On addition of Cl^-, the DPV peak centred at 0.74 V vs. Fc^+/Fc progressively decreases, and a new peak develops at 0.28 V vs. Fc^+/Fc. Such a peak is associated with the replacement of an MeCN molecule axially bound to the Ni^{III} centre by a Cl^- ion. The new peak reaches its maximum value after the addition of one equivalent of Cl^- (while the peak centred at 0.74 V disappears). Noticeably, addition of further equivalents of Cl^- (two and more) does not induce the development of any further peak at a less positive potential. This indicates that even in excess of chloride only the $[Ni^{III}(\mathbf{3})Cl]^{2+}$ species forms and that the bulky substituent prevents the addition of a second Cl^- ion. Thus, the oxidation process in presence of Cl^- can be described by the equilibrium given in Equation (5).

$$[Ni^{II}(\mathbf{3})]^{2+} + Cl^- \rightleftharpoons [Ni^{III}(\mathbf{3})Cl]^{2+} + e^- \qquad (5)$$

Cl^- binding to the Ni^{III} centre can be visually perceived and spectrophotometrically monitored on titration of an electrolysed solution of the $[Ni^{II}(\mathbf{3})]^{2+}$ complex. In particular, in a controlled potential electrolysis experiment on a 10^{-4} M solution of $[Ni^{II}(\mathbf{3})](ClO_4)_2$, the potential of the platinum gauze used as a working electrode was set at 0.85 V vs. Fc^+/Fc. 1.1 ± 0.1 mol of electrons per mol of complex were consumed. The solution took the green colour typically observed with the formation of Ni^{III} tetraaza-macrocyclic complexes. In particular, a charge-transfer ($N \rightarrow Ni^{III}$) absorption band developed at 320 nm ($\varepsilon = 4600\,M^{-1}cm^{-1}$), showing a shoulder at 380 nm ($\varepsilon = 3450\,M^{-1}cm^{-1}$). The electrolysed solution was then titrated with a standard MeCN solution of tetrabutylammonium chloride.

On Cl^- addition, the solution took on a bright yellow colour, and the spectrum was substantially modified. The family of spectra obtained during the titration is shown in Figure 3. In particular a limiting spectrum (a single broad band centred at 320 nm, $\varepsilon = 5600\,M^{-1}cm^{-1}$) was obtained after the addition of one equivalent of Cl^-. Further anion addition did not modify the spectrum. This behaviour is consistent with the formation of a five-coordinate species $[Ni^{III}(\mathbf{3})Cl]^{2+}$, as hypothesised on the basis of voltammetric titration experiments. The ε versus chloride equivalent profile (see inset in Figure 3) showed a sharp end-point, indicating the formation of a very stable adduct ($\log K > 10^7$).

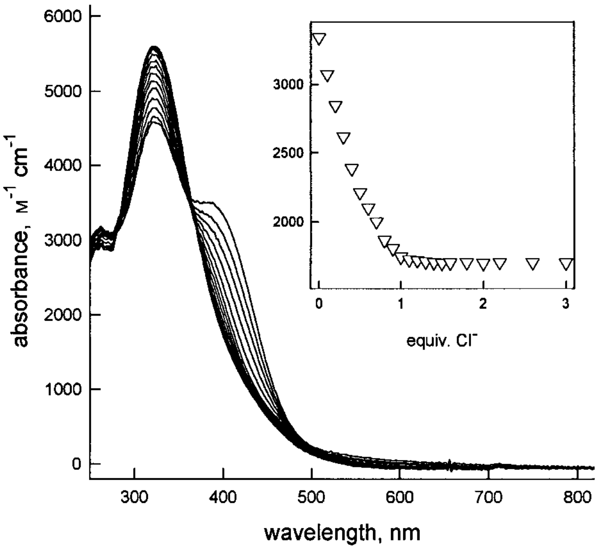


Figure 3. Spectrophotometric titration of an MeCN solution of $[Ni^{III}(\mathbf{3})]^{3+}$ with $[Bu_3Bz]Cl$. The solution of $[Ni^{III}(\mathbf{3})]^{3+}$ had been prepared through controlled potential electrolysis. The formation of the $[Ni^{III}(\mathbf{3})(Cl)]^{2+}$ species is monitored through the increase of the band at 320 nm and the decrease of the band at 400 nm. Inset: plot of the molar absorbance at 400 nm vs. the equivalents of Cl^-. The log*K* value for the equilibrium $[Ni^{III}(\mathbf{3})]^{3+} + Cl^- \rightleftharpoons [Ni^{III}(\mathbf{3})Cl]^{2+}$ is higher than 7.

NCO^- displays a similar behaviour. In fact, on anion addition a new DPV peak developed at a distinctly less positive potential (0.24 V vs. Fc^+/Fc), indicating strong interaction with the Ni^{III} centre. Also in this case, the DPV peak stopped increasing after the addition of one equivalent of NCO^-, and no further peaks developed on addition of an excess of the anion, indicating the formation of the five-coordinate species $[Ni^{III}(\mathbf{3})NCO]^{2+}$. However, addition of NCO^- to an MeCN solution of $[Ni^{III}(\mathbf{3})]^{3+}$, prepared through controlled potential electrolysis, caused decomposition of the trivalent complex. Thus, the $[Ni^{III}(\mathbf{3})NCO]^{2+}$ complex appears to be stable only in the time scale of the voltammetry experiment, whereas, on an extended time scale, the Ni^{III} centre oxidises the coordinated anion. Anion oxidation was even more evident with Br^- and NCS^- and was observed to take place also in the course of voltammetry studies. In fact, in presence of the anion the anodic discharge was anticipated and immediately followed the Ni^{II}-to-Ni^{III} oxidation wave.

The less donating HSO_4^- and NO_3^- anions were completely resistant to the oxidation, but were able to induce only a modest stabilisation of the Ni^{III} state. In particular, the anion-sensitive peak formed at a potential only 200 mV (HSO_4^-) and 120 mV (NO_3^-) less positive than that observed in absence of any coordinating anion. Titration with the anion of the electrolysed solution induced a neat modification of the spectrum. The absorbance versus anion equivalent profiles corresponded to the formation of a 1:1 adduct. However, the profiles were smooth enough to allow the determination of the anion binding constants: HSO_4^-, 4.2 ± 0.1 log units; NO_3^-, 3.6 ± 0.1.

Chloride translocation between metal centres hosted by the ditopic receptor 1: Due to its good coordinating tendencies and to its high resistance toward oxidation, Cl^- appears as the best candidate for being reversibly translocated in the $Cu^{II} \sim Ni^{II}$ dimetallic complex of **1**. Spectrophotometric titration experiments on an MeCN of the $Cu^{II} \sim Ni^{II}$ species, indicated that the anion seeks the Cu^{II} centre and that a 1:1 adduct, $Cu^{II}(Cl) \sim Ni^{II}$, forms. The constant associated to the complexation equilibrium ($\log K = 5.66 \pm 0.09$) guarantees that if one equivalent of anion is added, 95 % is bound to the Cu^{II}-tren subunit of the $Cu^{II} \sim Ni^{II}$ system (at a concentration 10^{-3} M).

The $Cu^{II} \sim Ni^{II}$ system undergoes a one-electron oxidation at 0.74 V vs. Fc^+/Fc in a 0.1 M Bu_4NClO_4 solution, as shown by DPV studies. On progressive addition of Cl^-, a new peak develops at a much less positive potential (0.24 V), while the intensity of the peak at 0.74 V progressively decreases. As observed in the case of the separate component $[Ni^{II}(\mathbf{3})]^{2+}$, the peak intensity reaches its maximum with the addition of one equivalent of Cl^-; further anion additions does not induce the appearance of any other peak. Again, this behaviour points towards the formation of a Ni^{III} five-coordinate subunit within the oxidised system $Cu^{II} \sim Ni^{III}$.

On exhaustive electrolysis on an MeCN solution 10^{-4} M of $Cu^{II} \sim Ni^{II}$ (potential of the working electrode set at 0.40 V vs. Fc^+/Fc), 0.9 ± 0.1 equivalents of electrons are consumed: the electrolysed solution displays the spectrum of a Ni^{III} tetramine chromophore. On titration with Cl^-, the absorption spectrum changes to that of a $[Ni^{III}(tetramine)Cl]^{2+}$ species. Quite interestingly, on addition of more than one equivalent of Cl^-, a charge-transfer band at 460 nm, typical of a Cu^{II}-tren-Cl subunit, develops. The increase of the band intensity stops with the addition of the second equivalent.

All the above evidence concurs with the occurrence of the translocation of the Cl^- ion from copper to nickel, following the Ni^{II}-to-Ni^{III} oxidation process. On Ni^{III}-to-Ni^{II} reduction, the anion goes back to the Cu^{II} centre. The redox-driven translocation between copper and nickel centres is pictorially sketched in Figure 4.

Back and forth anion translocation can be achieved under bulk conditions by carrying out controlled electrolysis experiments on an MeCN solution containing equimolar amounts of $Cu^{II} \sim Ni^{II}$ and Cl^-. Figure 5 shows the absorption spectrum of the reduced form, $Cu^{II} \sim Ni^{II}$. On electrolysis at a working electrode potential of 0.40 V, the band at 460 nm (corresponding to the Cu^{II}-(tren)-Cl fragment) disappears and a band at 315 nm develops (corresponding to the $[Ni^{III}(cyclam)Cl]^{2+}$ subunit, see Figure 5), while the solution turns from blue-green to yellow. If the potential of the platinum gauze is then set at 0.00 V, the solution turns blue-green again, while the spectrum of the reduced species is restored. The anion translocation between Cu^{II} and Ni^{III} can be carried out back and forth for several cycles with no destruction of the dimetallic system, as indicated by the fact that band intensities of the pertinent spectra remain unchanged.

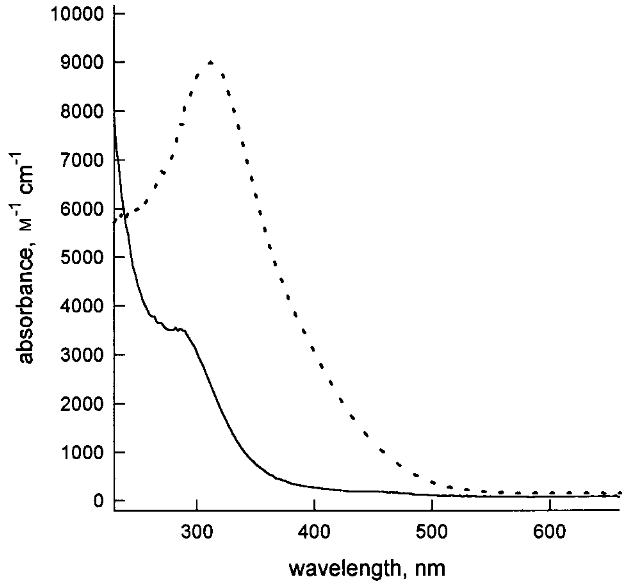


Figure 5. Spectrophotometrical monitoring of the electrochemically driven Cl^- translocation within the two-component system $[Cu^{II} \sim Ni^{II}]$. Solid line: spectrum of an MeCN solution containing equimolar amounts of $[Cu^{II} \sim Ni^{II}]$ and Cl^- before electrolysis; the anion stays on the Cu^{II} centre. Dotted line: spectrum of the same solution after electrolysis; Ni^{II} has been oxidised to Ni^{III} and the anion has moved to the Ni^{III} centre.

The *neat* intramolecular anion-translocation equilibrium: Let us now consider in detail the thermodynamic aspects of the anion-translocation process. In this context, a useful parameter to discuss is ΔE, the difference of the potentials of the Ni^{III}/Ni^{II} couple in absence and in presence of the anion. $\Delta E(6)$, which corresponds to the separation of the DPV peaks observed in the voltammetric profile obtained for a solution of $Cu^{II} \sim Ni^{II}$ containing a substoichiometric amount of X^- (e.g., 0.5 equiv.), is associated with the neat intramolecular anion-translocation equilibrium shown in Equation (6), in which X^- moves from Cu^{II} to the oxidised proximate metal centre, Ni^{III}.

In particular the driving force of the equilibrium in Equation (6) is given by: $\Delta G^o(6) = -F\Delta E(6)$, -11.5 kcal mol^{-1} when $X^- = Cl^-$. It is convenient to compare the equilibrium in Equation (6), which we consider an intramolecular process, with that in Equation (7), in which the X^- anion is neatly transferred through an inter-

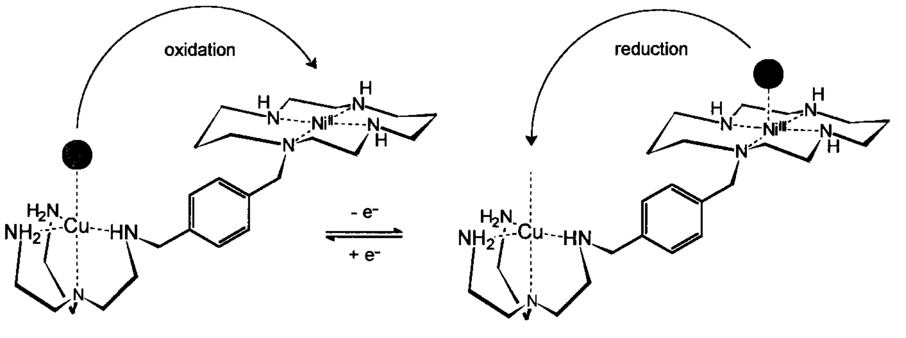


Figure 4. The reversible redox-driven translocation of an X^- ion between copper and nickel centres within the two-component system $[Cu^{II} \sim Ni^{II}]$.

$$[\mathrm{Cu^{II}(X)\sim Ni^{III}}]^{4+} \rightleftharpoons [\mathrm{Cu^{II}\sim Ni^{III}(X)}]^{4+} \quad (6)$$

$$[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+} + [\mathrm{Ni^{III}}(\mathbf{3})]^{3+} \rightleftharpoons [\mathrm{Cu^{II}}(\mathbf{2})]^{2+} + [\mathrm{Ni^{III}}(\mathbf{3})\mathrm{X}]^{2+} \quad (7)$$

molecular process from one separate component to the other. The corresponding $\Delta E(7)$ value was given by the separation of the two peaks appearing in the DPV profile obtained for a solution that contained equimolar amounts of $[\mathrm{Cu^{II}}(\mathbf{2})]^{2+}$ and $[\mathrm{Ni^{II}}(\mathbf{3})]^{2+}$, plus 0.5 equivalents of $\mathrm{X^-}$. $\Delta E(7)$ (0.17, for $\mathrm{X^-} = \mathrm{Cl^-}$) is distinctly smaller than $\Delta E(6)$ and $\Delta G^{\circ}(7)$ is remarkably less negative ($-4.0\ \mathrm{kcal\,mol^{-1}}$) than $\Delta G^{\circ}(6)$. This indicates that the neat anion-translocation process within the covalently linked two-component system $[\mathrm{Cu^{II}(X)\sim Ni^{III}}]^{4+}$ is strongly favoured with respect to the intermolecular transfer between the separate components, $[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+}$ and $[\mathrm{Ni^{III}}(\mathbf{3})]^{3+}$. The determination of ΔE for both equilibria in Equations (6) and (7) at varying temperature affords the evaluation of the Gibbs-Helmoltz equation terms ΔH° and $T\Delta S^{\circ}$.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -F\Delta E^{\circ} \quad (8)$$

$$(\mathrm{d}/\mathrm{d}T)\Delta E = \Delta S^{\circ}/F \quad (9)$$

In particular, the ΔE versus T plot must be linear and the straight-line slope gives access to the entropy change [Eq. (9)]. We observed that for the covalently linked system in an MeCN solution, $\Delta E(6)$ does not vary along the investigated temperature interval [(−15)–35 °C], indicating that $\Delta S^{\circ} = 0$ (see Figure 6). It follows that $\Delta G^{\circ} = \Delta H^{\circ} = -11.5\ \mathrm{kcal\,mol^{-1}}$.

Thus, the especially favourable free-energy change associated with the neat translocation equilibrium [Eq. (6)] is solely due to a very exothermic thermal contribution, which may reflect the stronger metal–ligand interactions involving $\mathrm{Ni^{III}}$ compared with $\mathrm{Cu^{II}}$. On the other hand, Figure 6 shows that $\Delta E(7)$ decreases linearly with the increasing temperature. The slope of the least-squares straight-line corresponds to a negative entropy change, $\Delta S^{\circ}(7)$, of $-27.8\ \mathrm{cal\,mol^{-1}\,deg^{-1}}$. The combination of $\Delta G^{\circ}(7)$ and $T\Delta S^{\circ}(7)$ values at 25 °C gives a $\Delta H^{\circ}(7)$ of $-12.3\ \mathrm{kcal\,mol^{-1}}$, which is comparable with $\Delta H^{\circ}(6)$. The closeness of enthalpy values for processes in Equations (6) and (7) is not unreasonable, as the balance of the bonding terms (breaking of the $\mathrm{Cu^{II}{-}X}$ bond and forming of the $\mathrm{Ni^{III}{-}X}$ bond) must be the same for both the covalently linked system and the two separate components. It follows that the great energy advantage experienced by the neat anion-translocation process in Equation (6) compared with that in Equation (7) is a mere entropy effect. None of the two investigated processes involve a change in the number of particles, which excludes the contribution of a translational term to the measured ΔS° values. We suggest that the very unfavourable entropy change associated with the equilibrium in Equation (7) has to be related to a probability effect.

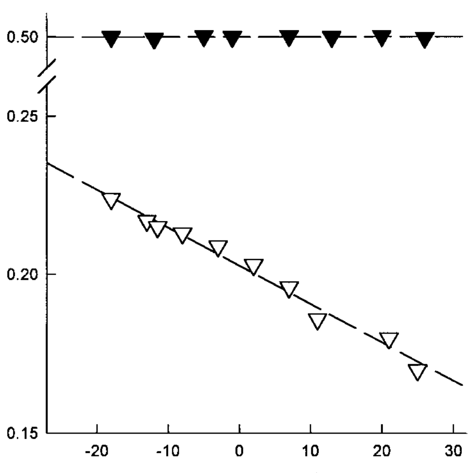


Figure 6. The variation of ΔE with the temperature for MeCN solutions i) of $[\mathrm{Cu^{II}\sim Ni^{II}}]$ (full triangles) and ii) of an equimolar mixture of $[\mathrm{Cu^{II}}(\mathbf{2})]^{2+}$ and $[\mathrm{Ni^{II}}(\mathbf{3})]^{2+}$ (open triangles), in presence of a substoichiometric amount of $\mathrm{Cl^-}$. ΔE values are associated to the neat anion-translocation equilibria given in Equations (6) and (7). The slope of the ΔE vs. temperature straight-line gives $\Delta S^{\circ}/F$.

In this context, one should consider that anion transfer, both in the covalently linked system $[\mathrm{Cu^{II}(X)\sim Ni^{II}}]^{4+}$ and in the equimolar mixture of the separate components $\{[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+} + [\mathrm{Ni^{III}}(\mathbf{3})]^{3+}\}$, results from the collision of a $\mathrm{Cu^{II}}$ bound $\mathrm{X^-}$ anion with a $\mathrm{Ni^{III}}$ centre. The probability that the collision takes place in the $\{[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+} + [\mathrm{Ni^{III}}(\mathbf{3})]^{3+}\}$ system is related to the concentration of the two separate components. The higher the concentration, the greater the probability that $[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+}$ and $[\mathrm{Ni^{III}}(\mathbf{3})]^{3+}$ collide, and the anion transfer takes place. On the other hand, in the case of $[\mathrm{Cu^{II}(X)\sim Ni^{III}}]^{4+}$, $\mathrm{X{-}Cu^{II}}$ and $\mathrm{Ni^{III}}$ are brought in contact through the occasional folding of the covalently linked system. By assuming that the $\mathrm{Cu^{II}{-}X}$ subunit moves within a sphere whose centre is the $\mathrm{Ni^{III}}$ centre and whose radius is the $\mathrm{Cu^{II}{-}Ni^{III}}$ distance (7.5 Å, as obtained from molecular modelling, from a semiempirical method; volume of the sphere $1766\ \text{Å}^3 = 1.766 \times 10^{-24}$ L), one could calculate an effective concentration of $\mathrm{X{-}Cu^{II}}$ of 0.94 M. Thus, the probability that such an intramolecular collision takes place is fixed, is independent upon the dilution and is much higher than that occurring in the $\{[\mathrm{Cu^{II}}(\mathbf{2})\mathrm{X}]^{+} + [\mathrm{Ni^{III}}(\mathbf{3})]^{3+}\}$ system (whose concentration ranged from 10^{-4} to 10^{-3} M, in typical electrochemical and spectroelectrochemical experiments). The previously described approach is strongly reminiscent of that devised by Gerold Schwarzenbach to interpret the chelate effect.[18] According to Schwarzenbach, the higher solution stability of a bidentate-ligand–metal complex with respect to its unidentate counterpart is related to the higher local concentration of the second donor atom of the chelating agent, which has just coordinated its first donor atom, compared with that of the second molecule of the unidentate ligand, which is dispersed in the solution.

The above considerations point to the main question of whether the redox-driven anion-translocation process [Eq. (1)] is intramolecular (in the sense that it is the $\mathrm{X^-}$ anion staying on $\mathrm{Cu^{II}}$ that moves to $\mathrm{Ni^{III}}$) or intermolecular ($\mathrm{X^-}$ goes from $\mathrm{Cu^{II}}$ to the solution, whereas a different $\mathrm{X^-}$ anion from the solution comes to $\mathrm{Ni^{III}}$). In this context, it should be noticed that system **1** has an open nature and the involved metal centres, $\mathrm{Cu^{II}}$, $\mathrm{Ni^{II}}$ and $\mathrm{Ni^{III}}$, are all labile. This implies that the metal-bound anion quickly exchanges with other X^- anions present in the solution (either unbound or bound to a metal). This is for instance the case of the copper bound Cl^- anion in the reduced form $[Cu^{II}(Cl) \sim Ni^{II}]^{3+}$. However, when the Ni^{II} centre is oxidised, the translocation of the Cl^- anion bound to the proximate Ni^{III} centre is the by far most probable event, several orders of magnitude more probable than the transfer from a different $[Cu^{II}(Cl) \sim Ni^{II}]^{3+}$ molecular system. In this sense, the process in Equation (1) has to be considered intramolecular.

Other anions and other metal centres: NCO^- displays a behaviour similar to that observed with Cl^-. It gives a stable adduct with the reduced form of the covalently linked system, $[Cu^{II}(NCO) \sim Ni^{II}]^{3+}$; the $\log K$ for the binding to Cu^{II} is 4.4 ± 0.1. Thus, in a solution that contains 10^{-3} M both of $Cu^{II} \sim Ni^{II}$ and NCO^-, 82 % of the anions are bound to Cu^{II}. Moreover, in the course of a DPV titration experiment, a new peak develops at 0.27 V vs. Fc^+/Fc and reaches its limiting value after the addition of one equivalent of NCO^-. $\Delta E(6)$ [0.47 V] is remarkably larger than $\Delta E(7)$ [0.26 V], confirming that the intramolecular anion translocation within the covalently linked system is much more favoured with respect to the intermolecular translocation between the separate components. However, NCO^- translocation takes place only in the time scale of the voltammetry experiment and cannot be carried out in a bulk electrolysis process, as a result of the decomposition of the oxidised species, $[Cu^{II} \sim Ni^{III}(NCO)]^{4+}$.

NO_3^- and HSO_4^- are as resistant to oxidation as Cl^-, but are not suitable for the redox-driven translocation process. In fact, they show a moderate affinity towards both Cu^{II} and Ni^{III} centres, as evidenced in the studies on the separate components. Thus, in a solution containing equimolar amounts of the dimetallic system and X^-, before and after oxidation, only a fraction of the anions are bound to the pertinent metal centre. Thus, the process in Equation (6) involves only a part of the added anions and may have an intermolecular character.

The effect of changing the metal centres was also verified. In particular we kept the same redox-active centre M_2 ($Ni^{II,III}$) and we replaced Cu^{II} with Zn^{II} as M_1. Zn^{II} has a pronounced tendency to form five-coordinate complexes. Specifically, Zn^{II} tetramine complexes have a good affinity towards the carboxylate donor group. Spectrophotometric titration experiments with the benzoate anion, $ArCOO^-$, on a solution of the $[Zn^{II} \sim Ni^{II}]^{4+}$ system in MeCN/MeOH (1:1 v/v) indicated the formation of a rather stable $[Zn^{II}(ArCOO) \sim Ni^{II}]^{3+}$ adduct ($\log K = 5.6 \pm 0.1$; the $N \rightarrow Zn^{II}$ charge-tranfer band was monitored). However, in DPV studies, we observed that, prior to the anion addition, a peak at 0.74 V vs. Fc^+/Fc was present (owing to Ni^{II}-to-Ni^{III} oxidation) and that the addition of up to one equivalent of $ArCOO^-$ induced neither the development of any new DPV peak at a lower potential nor a shift of the peak at 0.74 V. This indicates that the benzoate anion forms a more stable complex with the Zn^{II}-tren subunit than with the Ni^{III}-cyclam fragment. Thus, the required sequence of binding tendencies $M_2^{(n+1)+} > M_1 > M_2^{n+}$ is altered and the redox-induced anion-translocation process [Eq. (1)] cannot take place.

Conclusions

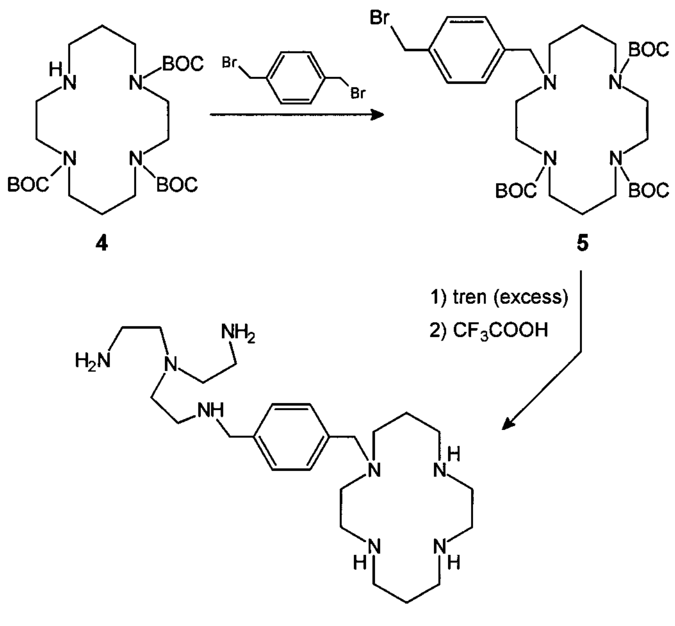
It has been shown that multicomponent systems suitable for the intramolecular translocation of anions between metal centres can be designed, by taking profit from the versatile stereochemical and redox behaviour of transition metals. The metal centres have to be labile and, when hosted by their own receptor, must be coordinatively unsaturated, thus, leaving room for the incoming anion. The ditopic system **1** combines two distinct tetramine fragments, tren and cyclam, which impose very different coordinative arrangements, trigonal bipyramidal and tetragonal, respectively. The receptor **1** operates very efficiently when Ni^{II} occupies the cyclam ring and Cu^{II} takes the tren compartment. Notice that the opposite combination of the metal centres (Ni^{II}-tren and Cu^{II}-cyclam) does not work at all for anion-translocation purposes. In fact, the Cu-cyclam subunit can operate as a redox device through the Cu^{II}/Cu^{III} change, which takes place at a high, but still attainable potential. However, the Cu^{III} centre, as a d^8 ion, tends to adopt a square-planar stereochemistry and displays no affinity towards the axial coordination by any X^- anion, thus failing the primary prerequisite for the occurrence of the redox-driven anion translocation, that is, that the $M_2^{(n+1)+}$ centre must display the highest affinity towards the X^- anion.

The investigated system has to be added to the list of bistable molecular systems, that is, molecules capable of existing in two states of comparable stability and of different topology. In such systems, the interchange from one state to the other should be kinetically feasible and should be controlled from the outside through a chemical, electrochemical or photochemical process. In systems of the type described here, each state is defined by the position of the X^- anion, whether on the M_1 or M_2 site. Switching from one state to the other is electrochemically driven and is fast and reversible in view of the open nature of the hosting framework and of the lability of the M–X bonds.

Experimental Section

Syntheses: The two component system **1** was obtained by the synthetic path outlined in Scheme 1. 1,4,8,11-tetraazacyclotetradecane (cyclam) was prepared according to literature methods.[19] *N,N′,N″*-tris(*tert*-butoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane (triBOCcyclam, **4**) was prepared through a modification[20] of a reported procedure.[21] All other reagents were commercially available and used as purchased (except where indicated in the experimental procedure). Mass spectra (ESI) were recorded on a Finnigan MAT TSQ 700 instrument, NMR spectra on a Bruker AMX 400 spectrometer.

***N,N′,N″*-Tris-(*tert*-butoxycarbonyl)-*N‴*-(4-bromomethyl)benzyl-1,4,8,11-tetraazacyclotetradecane** (**5**): TriBOCcyclam (**4**; 0.95 g, 1.90 mmol) was dissolved in toluene (60 mL) and allowed to react with 1,4-dibromomethylbenzene (0.51 g, 1.95 mmol) and Na_2CO_3 (0.35 g, 2.47 mmol) at the mixture reflux temperature, under a nitrogen atmosphere. After 24 hours, the mixture was filtered, and the solvent removed on a rotary evaporator. The semisolid crude product was purified on a silica gel column, with ethyl acetate/*n*-hexane (1:1 v/v) as eluent, to give the pure compound **5**, as a glassy white solid (0.58 g, 45 % yield; $R_f = 0.46$). ^1H NMR ($CDCl_3$): $\delta = 7.24$ (d, 2H; phenyl ring), 7.16 (d, 2H; phenyl ring), 4.4 (s, 2H; $ArCH_2Br$), 3.45 (s, 2H; $ArCH_2N$), 3.1–3.4 (m, 12H; $CONCH_2$), 2.58 (t, 2H; $NCH_2CH_2NCH_2Ar$), 2.37 (t, 2H; $ArCH_2NCH_2CH_2CH_2N$), 1.83 (q, 2H;



Scheme 1. Synthesis of the tren-cyclam conjugate **1**. BOC is the protecting group: tris-(*tert*-butoxycarbonyl).

CONCH$_2$C*H*$_2$CH$_2$NCO), 1.61 (q, 2H; ArNCH$_2$C*H*$_2$CH$_2$NCO), 1.41–1.29 (s, 27H; C(C*H*$_3$)$_3$); MS (ESI): 683, 685 [*M*$^+$+H].

***N*′-(2-Aminoethyl)-*N*-1-{2-[4-(1,4,8,11-tetraazacyclotetradecane-1-methyl)benzylamino]ethyl}ethane-1,2-diamine** (**1**): Compound **5** (0.400 g, 0.58 mmol) was dissolved in toluene (30 mL) and treated with *N,N′,N″*-tris-(2-aminoethyl)amine (tren, 0.45 mL, 0.432 g, 2.9 mmol) under a nitrogen atmosphere, at the reflux temperature. After 24 hours, the cooled reaction mixture was filtered and the solvent removed on a rotary evaporator. The oily residue was kept under high vacuum (0.1 Torr) for 48 hours at 50 °C, to eliminate the excess of tren. The obtained semisolid was then dissolved in CF$_3$COOH (30 mL) and kept well-stirred for 24 hours under a nitrogen atmosphere, to deprotect cyclam amino groups from the BOC group. CF$_3$COOH was then removed on a rotary evaporator, the residue dissolved in 10% HCl (30 mL) and extracted with CH$_2$Cl$_2$ (2×20 mL) to eliminate the *tert*-butanol formed from BOC after amine deprotection. The aqueous solution was then made basic with 6 M NaOH, extracted with CH$_2$Cl$_2$ (5×20 mL portions) and dried over Na$_2$SO$_4$. Removal of the solvent on a rotary evaporator gave **1** as a pure product (0.21 g, 80% yield). ^{1}H NMR (CDCl$_3$): $\delta = 7.20$ (d, 2H; phenyl ring), 7.12 (d, 2H; phenyl ring), 3.7 (s, 2H; NHC*H*$_2$Ar), 3.45 (s, 2H; ArC*H*$_2$N), 2.4–2.9 (m, 28H; CH$_2$ adjacent to amino groups), 1.81 and 1.70 (q and q, 2H + 2H; NHCH$_2$C*H*$_2$CH$_2$NH and NCH$_2$C*H*$_2$CH$_2$NH); MS (ESI): 449 [*M*$^+$+H].

[Ni^{II}Cu^{II}{*N*′-(2-aminoethyl)-*N*-1-{2-[4-(1,4,8,11-tetraazacyclotetradecane-1-methyl)benzylamino]ethyl}ethane-1,2-diamine}](ClO$_4$)$_4$·2H$_2$O·C$_2$H$_5$OH, (**[Ni^{II}Cu^{II}(1)](ClO$_4$)$_4$**·2H$_2$O·C$_2$H$_5$OH): Compound **1** (0.050 g, 1.11 mmol) was dissolved in CH$_3$OH (20 mL) and treated with a nickel(II) perchlorate solution in water (0.54 M, 0.206 mL, 0.111 mmol). The obtained solution was heated at reflux for 2 hours, after which time it took on a yellow-orange colour. Once cooled at room temperature, a copper(II) perchlorate solution in water (0.54 M, 0.202 mL, 0.110 mmol) was added, to give a green solution. After 20 minutes stirring at room temperature, the solvent was removed with a nitrogen stream to obtain a glass, which, on treatment with absolute ethanol (3 mL) gave [Ni^{II}Cu^{II}(**1**)](ClO$_4$)$_4$·2H$_2$O·C$_2$H$_5$OH as a grey-blue powder. C$_{26}$H$_{58}$N$_8$O$_{19}$Cl$_4$CuNi (1050.83): calcd C 29.73, H 5.52, N 10.66; found C 29.54, H 5.48, N 10.47; MS (ESI) 866, 868, 870, 872 [{[Ni^{II}Cu^{II}(**1**)](ClO$_4$)$_3$}$^+$].

[Ni^{II}{*N*-(4-*tert*-butyl)benzyl-1,4,8,11-tetraazacyclotetradecane}](ClO$_4$)$_2$ (**[Ni^{II}(3)](ClO$_4$)$_2$**): 1,4,8,11-Tetraazacyclotetradecane (cyclam, 1.5 g, 7.49 mmol mmol) was dissolved in hot toluene (50 mL), under a nitrogen atmosphere. 4-(*tert*-butyl)bromomethylbenzene (0.27 mL, 0.34 g, 1.5 mmol) was added, and the obtained solution kept at the reflux temperature for 2 hours, after which time a white precipitate of cyclam·HBr was formed. The mixture was allowed to cool to room temperature and the abundant precipitate (cyclam hydrobromide plus unreacted excess cyclam) was filtered off. The obtained clear solution was extracted with NaOH (0.1 M, 2×30 mL portions), in order to remove the remaining plain cyclam dissolved in toluene,and was dried over Na$_2$SO$_4$, and the solvent removed to give crude *N*-(4-*tert*-butyl)benzyl-1,4,8,11-tetraazacyclotetradecane (0.48 g, 92% yield). The ligand was dissolved in methanol (30 mL) and an aqueous solution of nickel(II) perchlorate (0.54 M, 2.50 mL, 1.35 mmol) was added. The obtained solution was heated to reflux for 2 hours, after which time a yellow-orange solution was obtained, which, on slow evaporation, gave [Ni^{II}(**3**)](ClO$_4$)$_2$, as an orange microcrystalline solid. Yield: 0.36 g (40%, based on 4-(*tert*-butyl)bromomethylbenzene). C$_{21}$H$_{38}$N$_4$Cl$_2$O$_8$Ni (604.15):calcd C 41.77, H 6.29, N 9.27; found C 41.60, H 6.25, N 9.30; MS (ESI): 603, 605, 607 [{[Ni^{II}(**3**)](ClO$_4$)$_2$}$^+$].

[Cu^{II}(*N*-benzyl-*N*′,*N*′-bis-(2-aminoethyl)ethylenediamine](ClO$_4$)$_2$·2H$_2$O (**[Cu^{II}(2)](ClO$_4$)$_2$·2H$_2$O**): *N,N′,N″*-Tris-(2-aminoethyl)amine (tren, 15 mL = 14.65 g, 100 mmol) was dissolved in toluene (50 mL) and treated with bromomethylbenzene (4.38 g, 25 mmol). The reaction mixture was heated at reflux, under a nitrogen atmosphere, for 8 hours, after which time an abundant white precipitate (tren hydrobromide) formed. The reaction mixture was allowed to cool to room temperature and was filtered, and toluene removed on a rotary evaporator, to give a mixture of the desired *N*-benzyl-*N*′,*N*′-bis-(2-aminoethyl)ethylenediamine ligand and excess tren, as a pale yellow oil. Excess tren was evaporated off under high vacuum (0.01 Torr, 130 °C) and the obtained brown oily residue was redissolved in CH$_2$Cl$_2$ and boiled for 2 hours in the presence of activated charcoal. After filtration and removal of CH$_2$Cl$_2$ on a rotary evaporator, pure *N*-benzyl-*N*′,*N*′-bis-(2-aminoethyl)ethylenediamine was recovered, as a pale yellow oil (5.2 g, 88% yield, based on bromomethyl benzene). ^{1}H NMR (CDCl$_3$): $\delta = 7.25$ (m, 5H; benzene ring), 3.70 (s, 2H; ArC*H*$_2$NH), 2.67 and 2.42 (t and t, 4H + 4H; N(C*H*$_2$CH$_2$NH$_2$)$_2$ and N(CH$_2$C*H*$_2$NH$_2$)$_2$), 2.62 and 2.50 (t and t, 2H + 2H; ArCH$_2$NHC*H*$_2$CH$_2$N and ArCH$_2$NHCH$_2$C*H*$_2$N). Complex [Cu^{II}(**2**)](ClO$_4$)$_2$·2H$_2$O was prepared by treating *N*-benzyl-*N*′,*N*′-bis-(2-aminoethyl)ethylenediamine (0.50 g, 2.12 mmol), dissolved in methanol, with an aqueous solution of Cu^{II} perchlorate (0.54 M, 3.92 mL, 2.12 mmol). The blue solution was allowed to react at room temperature for 30 minutes, and then the volume of the solvent was reduced to 5 mL on a rotary evaporator, which caused the separation of a blue oil, which, after decantation of the remaining solvent and treatment with diethyl ether gave [Cu^{II}(**2**)](ClO$_4$)$_2$·2H$_2$O, as a microcrystalline solid. C$_{13}$H$_{28}$N$_4$Cl$_2$CuO$_{10}$ (534.83): calcd C 29.21, H 5.23, N 10.47; found C 29.15, H 5.20, N 10.42.

Spectroelectrochemistry: UV/Vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Electrochemical measurements (cyclic voltammetry, CV, differential pulse voltammetry, DPV, controlled potential coulometry, CPC) were performed with a P.A.R. 273 potentiostat/galvanostat, under the control of a personal computer, with dedicated software. In CV and DPV studies, the working electrode was a platinum microsphere and the counter-electrode was a platinum foil. A platinum wire was used as a pseudoreference electrode and was calibrated against ferrocene as an internal standard. Thus, all the potentials reported in this work have been referred to the classical Fc$^+$/Fc (Fc = ferrocene) standard couple. CPC experiments were performed on solutions $2-5\times 10^{-4}$ M in the two-component system, with a platinum gauze as a working electrode. The counter-electrode compartment was separated from the working compartment by a U-shaped bridge, filled by an MeCN solution 0.1 M in [Bu$_4$N]ClO$_4$. The reference electrode, a platinum wire dipped in the working cell, was calibrated by a CV experiment prior to the electrolysis. The spectra of the electrolysed solution were taken by the use of a quartz fiber optical probe (Hellma, 661.500-QX), dipped in the working compartment and connected to the diode array spectrophotometer. The optical path of the probe was 2×10 mm. In the anion titration experiment, solutions of [Bu$_4$N]X salts were used (X = NCO, HSO$_4$, NO$_3$), with the exception of [BzBu$_3$N]Cl. The constants for the $M^{n+} + X^- \rightleftharpoons [MX]^{(n-1)+}$ equilibria were calculated by processing the data of spectrophotometric titration experiments performed on solutions containing M^{n+} (5×10^{-4}–10^{-3} M concentration range), thermostatted at 25 °C, titrated with solutions of the pertinent ammonium salt. In each titration, 20–30 points were recorded, and data refined through the HYPERQUAD package, which minimizes a least-squares function.[22]

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