Electrochemically Switched Anion Translocation in a Multicomponent Coordination Compound

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Complex [**3a**]$^{2+}$ has been synthesized, which contains one Ni^{II} cyclam-like and one bipyridine fragment (cyclam = 1,4,8,11-tetraazacyclotetradecane). Spectrophotometric and potentiometric titration experiments in aqueous solution demonstrated that in the examined pH range (2−10), the Ni^{II} cyclam-like subunit remains square planar, i.e., it does not interact with the bipyridine unit, which is instead allowed to bind external metal centers. In particular, in the presence of 0.5 equiv of Cu^{II}, the trinuclear multicomponent coordination compound [Cu^{II}(**3a**)$_2$-(H$_2$O)]$^{6+}$ is the only species existing in solution over a wide pH range. The water molecule bound to the Cu^{II} center can be substituted by inorganic anions, forming [Cu^{II}(**3a**)$_2$(anion)]$^{5+}$ species, and the binding constants of a series of mononegative anions have been determined, demonstrating the effectiveness of [Cu^{II}(**3a**)$_2$(H$_2$O)]$^{6+}$ as an anion receptor. Voltammetric experiments have shown that the two Ni^{II} centers in [Cu^{II}(**3a**)$_2$(H$_2$O)]$^{6+}$ can be reversibly oxidized to Ni^{III}, a d^7 cation which needs further coordination in its axial positions. In the case of the [Cu^{II}(**3a**)$_2$(anion)]$^{5+}$ species, differential-pulse voltammetry experiments demonstrated that on oxidation of the peripheral Ni^{II} centers, the anion bound to the central Cu^{II} cation jumps onto one of the peripheral Ni^{III} centers. Thus, the translocation of an anion from the center to the periphery (and vice versa) can be electrochemically switched for the multicomponent coordination compound considered here.

Introduction

Positional changes of atoms in a molecular system have been proposed to correspond to a mechanical process at a molecular level.[1] Triggering of these processes by means of a switch (chemical, electrochemical, or photochemical) represents the first step in the chemical transformation of energy into controlled oriented motion.

The literature offers few examples of this kind. In particular, the photochemically controlled threading/unthreading of a pseudorotaxane[2] and the electrochemically triggered swinging of a [2]-catenate[3] have been reported. Moreover, the electrochemically controlled translocation of a copper ion from one compartment to the other of a ditopic asymmetric macrotricycle has been proposed,[1] and the hopping of an iron cation between two different coordination sites in a multicomponent system has been recently reported[4] (the processes being driven by the different affinity of copper in the I or II oxidation state and iron in the II or III oxidation state toward the compartments of the ligands). Finally, some examples of electrochemically induced molecular hysteresis have been demonstrated.[5] In all cases, bistability is an essential prerequisite and, in particular, one part of the molecular system must display different

coordinative preferences[1,3−5] or give donor−acceptor interactions of different energies[2] in the two states.

A nickel cation coordinated to a cyclam-like macrocyclic tetraamine ligand (cyclam = 1,4,8,11-tetraazacyclotetradecane) gives rise to a bistable system. In fact, both the [Ni(cyclam)]$^{2+}$ and [Ni(cyclam)]$^{3+}$ species are kinetically inert and thermodynamically stable under a wide range of conditions,[6] and it is possible to go back and forth from one oxidation state to the other through fast and reversible chemical or electrochemical redox processes. Moreover, while the Ni^{II} (d^8) cation encircled by a cyclam-like macrocycle is usually low spin and adopts a square planar geometry (the available coordination sites being occupied by the tetraamine macrocyclic ligand), the low-spin d^7 Ni^{III} cation prefers octahedral coordination and binds, when incorporated in the cyclam ring, two more ligands in its axial positions. We wished to profit from the Ni^{II}/Ni^{III} redox change in a cyclam environment to generate a multicomponent system suitable for the intramolecular translocation of an anion, driven by the variation of the redox potential.

Following the *coordinative approach* for the construction of supramolecular coordination compounds,[7] we first appended a bipyridine unit to a Ni^{II} cyclam-like complex, thus obtaining the component [**3a**]$^{2+}$ (Scheme 1), and then bound two of these components, through their bpy (bpy = bipyridine) subunit, to a Cu^{II} cation, thus forming the multicomponent coordination complex [Cu^{II}(**3a**)$_2$(H$_2$O)]$^{6+}$.

While the Ni^{II} centers in this multicomponent molecule are insensitive to the addition of anions, the [Cu^{II}(R-bpy)$_2$]$^{2+}$

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Scheme 1
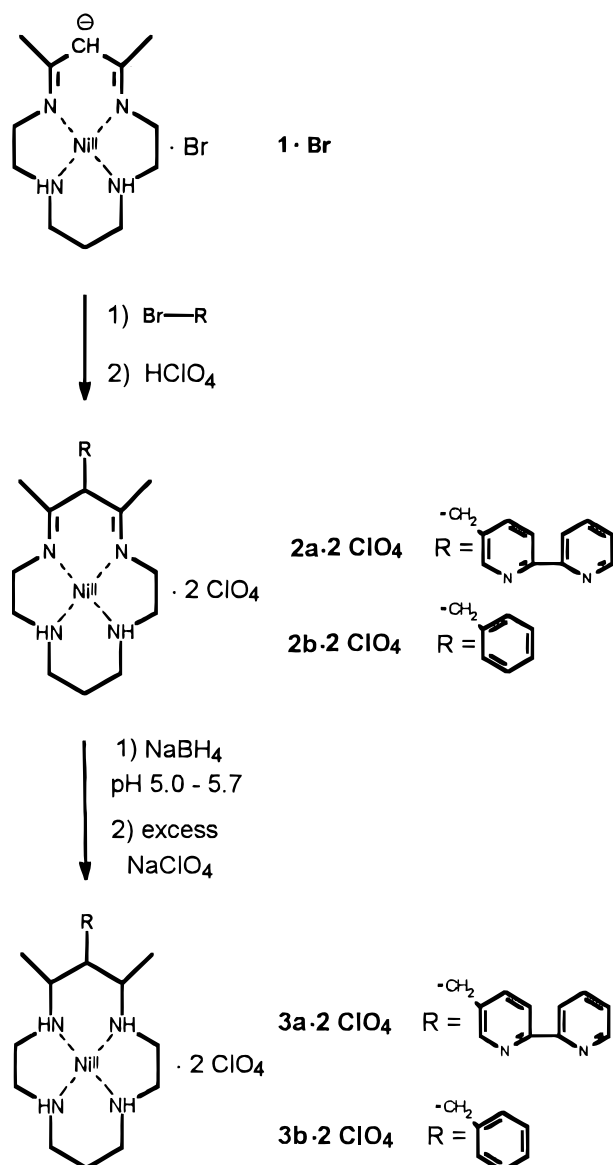
fragment binds anions like N_3^-, NCO^-, NCS^-, and OH^- with a 1:1 stoichiometry. However, when the oxidation state of the nickel cation is changed from II to III, the Ni^{III} centers show much more affinity than those of Cu^{II} toward anionic species; thus, the anion bound to the central Cu^{II} ion jumps onto one of the peripheral Ni^{III} ions. Conversely, reduction of Ni^{III} to Ni^{II} makes the anion move back to the Cu^{II} center. In this regard, the multicomponent species $[Cu^{II}(3a)_2(anion)]^{5+}$ allows the electrochemically switched translocation of an anion from the center to the periphery (and vice versa) of the system.

This work describes the synthesis and the solution behavior of the component $[3a]^{2+}$, its coordinative tendencies toward Cu^{II} in aqueous solution, and the ability of the multicomponent species $[Cu^{II}(3a)_2(H_2O)]^{6+}$ to bind anions. Electrochemical experiments on both the multicomponent complex and its separate components demonstrated the effectiveness of the translocation process.

Experimental Section

5-Methyl-2,2′-bipyridine,[8] 5-(bromomethyl)-2,2′-bipyridine,[9] and (2,4-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,4-dienato)nickel(II) bromide

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(**1·Br**)[10] have been prepared according to literature methods.

[Ni^{II}(3-(3-bipyridinylmethyl)-2,4-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,4-diene)](ClO₄)₂·HClO₄(2a·(ClO₄)₂·HClO₄). (2,4-Dimethyl-1,5,8,12-tetraazacyclotetradeca-1,4-dienato)nickel(II) bromide (1.65 g, 4.6 mmol) (**1·Br**) was partly dissolved in 100 mL of absolute ethanol, to which 1.14 g (4.6 mmol) of 5-(bromomethyl)-2,2′-bipyridine was added as a solid. The reaction mixture was refluxed for 16 h, under a dinitrogen atmosphere, during which time all of the material dissolved while the color of the solution changed from purple to orange-brown. The volume of the solution obtained was reduced to 70 mL *in vacuo*, and concentrated (70%) perchloric acid was added dropwise, until precipitation of the lemon-yellow powdery product was complete. Recrystallization from an ethanol/1 M HClO₄ solution (70:30 in volume) gave 2.5 g of crystalline **2a·(ClO₄)₂·HClO₄** (yield 72%). Anal. Calcd for $C_{23}H_{32}N_6Cl_3O_{12}Ni$: C, 36.82; H, 4.39; N, 11.19. Found: C, 36.60; H, 4.41; N, 11.10. IR (cm⁻¹): 3211 (NH), 1649 (C=N), 1588, 1575, 1557 (CH of the bipyridine rings). MS (ESI): 549 ([**2a·**ClO₄]⁺).

[Ni^{II}(3-(3-bipyridinylmethyl)-2,4-dimethyl-1,5,8,12-tetraazacyclotetradecane)](ClO₄)₂ (3a·(ClO₄)₂). **2a·**(ClO₄)₂·HClO₄ (2.0 g, 2.66 mmol) was dissolved in 150 mL of an aqueous 0.1 M pyridine/HCl buffer (pH = 5.1). NaBH₄ (1.5 g, 40 mmol) was added in small portions; the pH of the solution was constantly monitored by means of a pH meter. Whenever the pH reached 5.7, the original value was restored by the addition of few drops of concentrated (37%) HCl. When the addition was complete, the obtained orange-pink solution was warmed to 70 °C for 2 h, then the hot solution was treated with 6 M NaOH until the pH reached the value of 7. Solid NaClO₄ was then added until the solution became cloudy. When the solution was cooled to room temperature, 0.86 g (yield 48%) of **3a·**(ClO₄)₂·H₂O was obtained as a pink-orange powder. Anal. Calcd for $C_{23}H_{38}N_6Cl_2O_9$-Ni: C, 41.12; H, 5.65; N, 12.50. Found: C, 41.03; H, 5.60; N, 12.54. IR (cm⁻¹): 3200 (NH), 1588, 1575, 1557 (CH of the bipyridine rings). MS (ESI): 553 ([**3a·**ClO₄]⁺).

[Ni^{II}(3-benzyl-2,4-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,4-diene)]Br₂ (2b·Br₂). **1·**Br (1 g, 2.76 mmol) was partly dissolved in 50 mL of absolute ethanol. Benzyl bromide (0.47 g, 2.76 mmol) was added, and the solution was warmed to reflux for 4 h, after which time a lemon-yellow precipitate formed. When the solution was cooled, more crystalline **2b·**Br₂ formed. Yield: 0.8 g (54%). Anal. Calcd for $C_{19}H_{30}N_4Br_2Ni$: C, 42.84; H, 5.63; N, 10.51. Found: C, 42.79; H, 5.61; N, 10.50. IR (cm⁻¹): 2230 (NH), 1650 (C=N).

[Ni^{II}(3-benzyl-2,4-dimethyl-1,5,8,12-tetraazacyclotetradecane)](ClO₄)₂ (3b·(ClO₄)₂). The synthesis of this compound followed the same procedure as for **3a·**(ClO₄)₂. Starting from 0.5 g (1.38 mmol) of **2b·**Br₂, 0.3 g of **3b·**(ClO₄)₂·(H₂O) was obtained as an orange-pink powder (yield 58%). Anal. Calcd for $C_{19}H_{36}N_4Cl_2O_9Ni$: C, 38.43; H, 6.06; N, 9.43. Found: C, 38.40; H, 6.09; N, 9.45. IR (cm⁻¹) 3200 (NH). MS (ESI): 475 ([**3a·**ClO₄]⁺).

Potentiometric titrations on complex $[3a]^{2+}$ (as its perchlorate salt) and on 5-methyl-2,2′-bipyridine, in the absence and in the presence of Cu^{II} ions (as perchlorate salt), were carried out through the use of an automatic system controlled by a PC. The temperature was mantained at 25 ± 0.1 °C, and each titration was performed on a solution of 50 mL, adjusted to a 0.1 M ionic strength with NaClO₄. The concentration of $[3a]^{2+}$, 5-methyl-2,2′-bipyridine, and the Cu^{II} cation were in the $(0.5-0.7) \times 10^{-3}$ M range. The titrant was a carbon dioxide free 0.2009 M NaOH solution, which had been standardized against potassium hydrogen phthalate. The glass electrode was calibrated using the Gran method.[11] Each titration consisted of 50–100 data points.

Spectrophotometric titrations on $[Cu^{II}(3a)_2(H_2O)]^{6+}$ and on $[Cu^{II}(5\text{-}methyl-2,2′-bipyridine)_2(H_2O)]^{2+}$ were carried out on 20 mL solutions, buffered at pH 5.9 by means of a 0.1 M $CF_3SO_3H/2,6$-lutidine buffer. One centimeter quartz cells were employed, thermostatted at 25 °C. The concentrations of the complexes were in the $1.0-3.0 \times 10^{-3}$ M range. Titrations were performed by microadditions (10–20 μL) of solutions containing the appropriate anion (concentrations were in the 0.1–0.5 M range).

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Data for both the potentiometric and spectrophotometric titrations were processed using the HYPERQUAD software package.[12]

UV−vis spectra were recorded on a Hewlett-Packard 8452A diode-array spectrophotometer, IR spectra were obtained on a Perkin-Elmer 1300 infrared spectrophotometer, and mass spectra (ESI) were recorded on a Finnigan MAT TSQ 700 instrument.

Differential-pulse voltammetry (DPV) measurements were performed in a conventional three-electrode cell, thermostatted at 25 °C through circulating water, with 0.1 M $NaClO_4$ as the supporting electrolyte, using a PAR 273 potentiostat/galvanostat controlled by a PC and driven by dedicated software. The pulse width in the DPV experiments in any case was 10 mV. A saturated calomel electrode, connected to the cell through a salt bridge filled with NaCl solution, was used as the reference electrode. A carbon paste working electrode was employed. The potential scan rate in the DPV experiments was 2 mV s^{-1}.

Results and Discussion

Design of the Multicomponent System. In the perspective of the preparation of C-functionalized cyclam-like tetraaza macrocycles, the use of the "dienato" Ni^{II} complex [**1**]$^+$ offers many advantages, with respect to the usual multistep synthetic routes.[13] The preparation of the bipyridine- and benzyl-substituted Ni^{II} complexes [**3a**]$^{2+}$ and [**3b**]$^{2+}$ benefits from the nucleophilicity of the deprotonated CH$^-$ moiety of [**1**]$^+$.[14] The nucleophilic substitution of Br$^-$ in 5-(bromomethyl)-2,2′-bipyridine and benzyl bromide proceeds smoothly, and the perchlorates of the diene derivatives [**2a**]$^{2+}$ and [**2b**]$^{2+}$ can be obtained with a one-step reaction, in high yields. However, the reduction of the imine bonds to obtain [**3a**]$^{2+}$ and [**3b**]$^{2+}$ must be done with care. Diene derivatives like [**2a**]$^{2+}$ and [**2b**]$^{2+}$ tend to lose the proton of the functionalized −CH(R)− carbon atom at pH values >7, giving a dienate form resembling [**1**]$^+$, and the action of NaBH$_4$ on these species is destructive. Therefore, reductions must be carried out in buffered aqueous solutions, and the pH value must be continuously checked and adjusted during the addition of the borohydride. Morever, in some syntheses, reduction was not complete, as revealed by the IR spectra on the solid, isolated products: in these cases, a residual imine band, centered at 1630 cm^{-1}, was found, due to the presence of some of the product still containing one C=N bond (as confirmed by mass analysis). In these cases, the product had to be subjected to a second reductive treatment, which eventually gave the pure [**3a**]$^{2+}$ and [**3b**]$^{2+}$ perchlorate salts.

It is worth noting that reduction of the imine bonds generates two asymmetric centers at the methyl-bearing carbon atoms of the macrocyclic ring. All of the attempts to separate the possible diastereomers were unsuccessful. In particular, when passing an aqueous solution of products [**3a**]$^{2+}$ or [**3b**]$^{2+}$ through a Sephadex SP-C25 column, only one band was eluted, which suggested that the obtained saturated macrocyclic complexes contain only one of the diastereomers, as has already been observed[15] for closely related molecules.

It should be noted that a 5-substituted 2,2′-bipyridine has been chosen for simple geometric considerations insofar as when appended to the Ni^{II} cyclam-like complex as in [**3a**]$^{2+}$, substitution in the 5-position prevents the coordination of the N atoms of the bpy fragment to the encircled Ni^{II} cation. On the other hand, the bulky substituent in the 5-position is sufficiently far

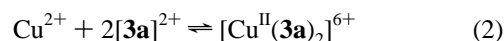away from the bpy donor set to allow the coordination to an "external" metal cation.

Solution Behavior of Complex [3a]$^{2+}$. Potentiometric titration experiments with standard base on aqueous solutions containing the bipyridine-functionalized Ni^{II} tetraamine complex [**3a**]$^{2+}$ and excess perchloric acid allowed for the determination of the protonation constant of the appended bpy unit (log $K = 4.37 \pm 0.02$), corresponding to the equilibrium

$$[\textbf{3a}]^{2+} + H^+ \rightleftharpoons [\textbf{3aH}]^{3+} \qquad (1)$$
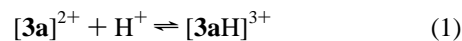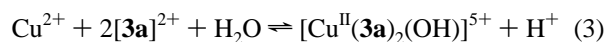
The obtained value is to be compared with that found under the same experimental conditions for 5-methyl-2,2′-bipyridine, for which a protonation constant of 4.76 ± 0.02 log units was calculated. The considerably lower value that was observed for the bipyridine fragment bearing a Ni^{II} macrocyclic complex may depend upon the electrostatic repulsive effect exerted by the proximate Ni^{2+} cation on the incoming proton.

The UV−vis spectra of aqueous solutions containing [**3a**]$^{2+}$ showed only one band, centered at 464 nm ($\epsilon = 40$ M^{-1} cm^{-1}), over the whole 2−10 pH range. This band corresponds to a square planar-coordinated, low-spin Ni^{II} cation,[16] and this demonstrates that even when the appended bipyridine subunit is not protonated, it is unable to further coordinate the Ni^{II} cation that is encircled in the macrocyclic ligand. Thus, the bipyridine donor set is available for the coordination of a second, external metal cation, an essential prerequisite[17] for the formation of supramolecular (or multicomponent) coordination compounds.

Interaction of [3a]$^{2+}$ with Cu^{II}. Potentiometric titration experiments with a standard base over the pH range 2−10, on solutions containing [**3a**]$^{2+}$ and Cu^{II} in a 2:1 molar ratio plus excess acid, demonstrated the formation of multicomponent complexes, involving the coordination of the bpy unit to the copper cation, and allowed for the calculation of the relative equilibrium constants. [Cu^{II}(**3a**)$_2$]$^{6+}$ and [Cu^{II}(**3a**)$_2$(OH)]$^{5+}$ are the only multicomponent species which form under these conditions. The relative formation constants are 11.48 ($\pm$0.02) and 3.90 ($\pm$0.02) log units, respectively, and correspond to the equilibria

$$Cu^{2+} + 2[\textbf{3a}]^{2+} \rightleftharpoons [Cu^{II}(\textbf{3a})_2]^{6+} \qquad (2)$$

and

$$Cu^{2+} + 2[\textbf{3a}]^{2+} + H_2O \rightleftharpoons [Cu^{II}(\textbf{3a})_2(OH)]^{5+} + H^+ \quad (3)$$

[Cu^{II}(**3a**)$_2$]$^{6+}$ is actually the only existing species (>95%) between pH 4 and 6, while at pH values >6, [Cu^{II}(**3a**)$_2$(OH)]$^{5+}$ begins to form, going over 95% at pH 9 (a distribution diagram can be found in the Supporting Information).

In the multicomponent coordination complex [Cu^{II}(**3a**)$_2$]$^{6+}$, a trigonal bipyramidal coordination can be assigned to the Cu^{II} cation (a water molecule completing the coordination polyhedron), in analogy to what is observed for Cu^{II} complexes with two plain[18] or substituted[19] bipyridine ligands. Moreover, [Cu^{II}-(**3a**)$_2$]$^{6+}$ displays a visible spectrum similar to that of a trigonal bipyramidal five-coordinate Cu^{II} species, like those found in

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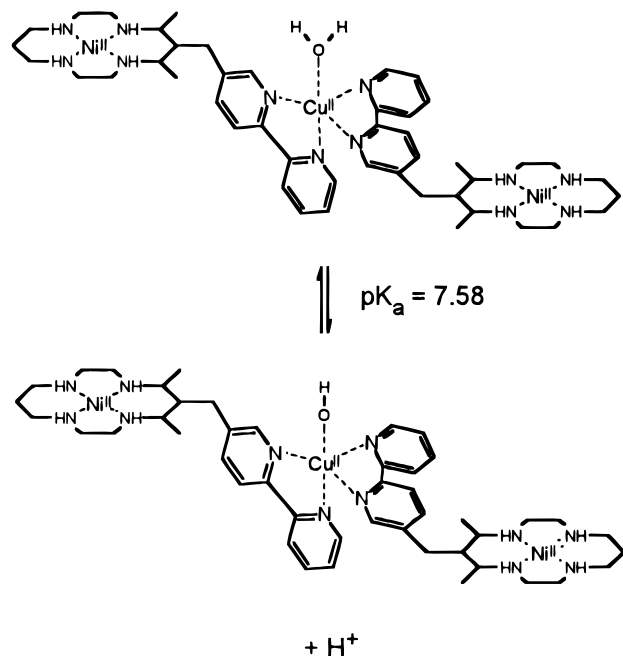
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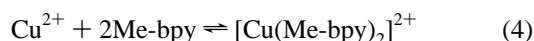(19) Burke, P. J.; Henrik, H.; Mc Millin, D. R. *Inorg. Chem.* **1982**, *21*, 1881
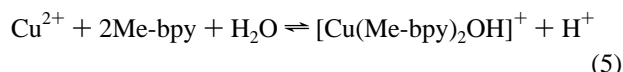
Scheme 2

Figure 1. Spectrophotometric titration of $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ with N_3^- (0−2.0 equiv of added anion; concentration of the multicomponent species is 1×10^{-3} M). Each spectrum corresponds to the addition of 0.2 equiv of N_3^-, which induces the growth of the intensity of the bands centered at 370 and 670 nm.

bis(tren) cage complexes[20] (tren = N,N',N''-tris(2-aminoethyl)-amine), showing a band centered at 700 nm and a large shoulder between 720 and 820 nm (the characteristic band assigned to square planar Ni^{II} remains at 460 nm). On this basis, $[Cu^{II}(\mathbf{3a})_2]^{6+}$ should be more correctly formulated as $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$.

The $[Cu^{II}(\mathbf{3a})_2(OH)]^{5+}$ species forms by deprotonation of the water molecule coordinated to the copper cation (Scheme 2), with a pK_a value of 7.58, as confirmed by coupled spectrophotometric/potentiometric titration experiments. In fact, while the spectrum of a solution containing $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ remains unchanged between pH 4 and 6.2, at pH > 6.2 (when $[Cu^{II}(\mathbf{3a})_2(OH)]^{5+}$ starts to form), the band assigned to the Cu^{II} chromophore begins to change, its maximum progressively shifting toward lower wavelengths and reaching a minimum value of 625 nm at pH 9.0 (>95% of $[Cu^{II}(\mathbf{3a})_2(OH)]^{5+}$).

Interestingly, potentiometric titrations and spectrophotometric experiments on the reference system Cu^{2+}/5-methyl-2,2'-bipyridine (Me-bpy) in a 1:2 molar ratio, revealed a parallel behavior. Two species are found in the 2−11 pH range, $[Cu^{II}(Me-bpy)_2]^{2+}$ and $[Cu^{II}(Me-bpy)_2OH]^+$, with formation constants of 11.78 and 2.97 log units, respectively, corresponding to the equilibria

$$Cu^{2+} + 2Me\text{-bpy} \rightleftharpoons [Cu(Me\text{-bpy})_2]^{2+} \tag{4}$$

and

$$Cu^{2+} + 2Me\text{-bpy} + H_2O \rightleftharpoons [Cu(Me\text{-bpy})_2OH]^+ + H^+ \tag{5}$$

The visible spectrum of aqueous solutions of $[Cu^{II}(Me-bpy)_2]^{2+}$ in the pH range 4−7 is almost identical to that of $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ (the band at 460 nm is of course missing), with a maximum centered at 710 nm and a broad shoulder between 730 and 820 nm, as expected for a Cu^{II} trigonal bipyramidal five-coordinate cation. Thus, it can be again assumed that the fifth coordination position is occupied by a water molecule and the species involved should be written as $[Cu(Me-bpy)_2(H_2O)]^{2+}$. From the potentiometric data, it can be seen that
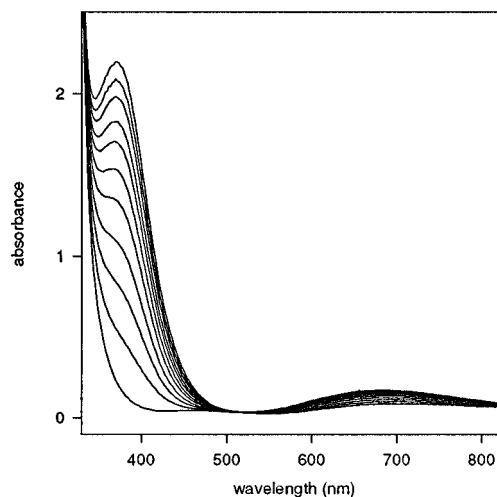
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$[Cu(Me-bpy)_2(H_2O)]^{2+}$ is the only species present in solution in the 4.5−7.5 pH range (a distribution diagram is deposited in the Supporting Information). Moreover, a shift of the visible band is observed from pH 7.5, which reaches the minimum value of 670 nm at pH 10.5. This process corresponds to the formation of $[Cu(Me-bpy)_2OH]^+$ from $[Cu(Me-bpy)_2(H_2O)]^{2+}$, i.e., to the deprotonation of the coordinated water molecule, for which a pK_a value of 8.81 can be calculated from the potentiometric data. Comparing this latter value with that found for $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ (pK_a = 7.58), it can be noted that the deprotonation of the coordinated water molecule is much easier (1.2 log units) in the multicomponent system than in $[Cu(Me-bpy)_2(H_2O)]^{2+}$. This can be ascribed to the presence of two positively charged Ni^{2+} centers in close proximity to the $[Cu^{II}(R-bpy)_2(H_2O)]^{2+}$ fragment, which favors the release of a proton by electrostatic repulsion. From a different point of view, one could say that the copper center in $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ binds the OH^- anion better than the copper center in $[Cu^{II}(Me-bpy)_2(H_2O)]^{2+}$.

$[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ as an Anion Receptor. The ability of the multicomponent system $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ to bind anions other than OH^- at its Cu^{II} center has been investigated through spectrophotometric titration experiments carried out on solutions containing Cu^{2+} and $[\mathbf{3a}]^{2+}$ in a 1:2 molar ratio, buffered at pH 5.9 (>95% of $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$); a 2,6-lutidine/$CF_3SO_3H$ buffer was chosen, in order to avoid any competition of the buffer components for the coordination at the fifth position of the copper center. Titration with standard solutions of a series of anions gave rise to drastic changes of the original spectrum both in the 650−800 nm (Cu^{II} d−d transitions) and in the 300−350 nm (charge transfer) regions. The profiles of the spectrophotometric titrations corresponded, in most cases, to the formation of a 1:1 complex, according to the equilibrium

$$[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+} + A^- \rightleftharpoons [Cu^{II}(\mathbf{3a})_2(A)]^{5+} + H_2O \tag{6}$$
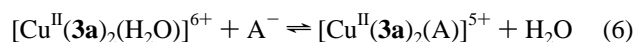
(A^- = anion). The result of a typical titration experiment obtained for the N_3^- anion is shown in Figure 1, which displays, in this case, the growth of a strong $Cu^{II}-N_3^-$ LMCT band, centered at 370 nm. Least-squares treatment of the titration data[12] has yielded the logarithmic binding constants for N_3^- (3.0 ± 0.1), NCO^- (2.4 ± 0.1), NCS^- (2.5 ± 0.1), NO_3^- (1.8 ± 0.1), and I^- (1.9 ± 0.1), while for other anionic species (Cl^-,

Br⁻), the titration profiles showed an almost linear absorbance increment in the examined range (0−5 equiv of added anion), which prevents an accurate determination of the binding constant (log $K \ll 2.0$).

These data are to be compared with those found for the reference complex $[Cu^{II}(Me\text{-}bpy)_2(H_2O)]^{2+}$ under the same conditions (pH = 5.9, 2,6-lutidine/CF₃SO₃H buffer). In all cases, the spectrophotometric data revealed almost linearly increasing titration profiles (i.e., log K values ≪2.0), except in the case of NCS⁻ (log $K = 2.13 \pm 0.1$ for the equilibrium $[Cu^{II}\text{-}(Me\text{-}bpy)_2(H_2O)]^{2+}$ + NCS⁻ ⇌ $[Cu^{II}(Me\text{-}bpy)_2(NCS)]^+$ + H₂O).

In addition to what is obtained for the OH⁻ anion (*vide supra*), these data indicate that the multicomponent coordination complex $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ displays a much higher binding tendency toward anions than the reference complex $[Cu^{II}(Me\text{-}bpy)_2(H_2O)]^{2+}$. This may be due to the presence of two positively charged Ni^{II} centers in close proximity to the Cu^{II} complex. Finally, it must be stressed that the spectrophotometric titrations on the isolated Ni^{II} cyclam-like reference fragment (i.e., the benzylic complex $[\mathbf{3b}]^{2+}$), with the complete series of the examined anions (pH = 5.9, CF₃SO₃H/2,6-lutidine buffer), did not modify the spectrum, even after the addition of 4−5 equiv of the anionic species, demonstrating that the low-spin Ni^{II} centers, in these complexes, do not show any affinity toward the anions considered.

Electrochemistry and Anion Translocation. The electrochemical behavior of the multicomponent species $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ and of its separate components $[Cu^{II}(Me\text{-}bpy)_2]^{2+}$ and $[\mathbf{3b}]^{2+}$ has been studied by means of voltammetric studies in 0.1 M NaCF₃SO₃ aqueous solutions; the pH was adjusted to 5.9 (>95% of $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ and $[Cu^{II}(Me\text{-}bpy)_2]^{2+}$) with standard NaOH.

A solution of the multicomponent complex was titrated with solutions of the anions examined (NCO⁻, N₃⁻, NCS⁻, NO₃⁻, Cl⁻) and a voltammetric experiment was carried out after each addition (in the case of Br⁻ and I⁻, the oxidation of the added anion was observed).

In the case of the $[Cu^{II}(Me\text{-}bpy)_2]^{2+}$ complex, no waves were found in the examined potential range (0.0 < E < 1.0 *vs* SCE), both in the presence of the background electrolyte alone and after the addition of up to 5 equiv of anions. As expected, under these conditions and in this potential range, $[Cu^{II}(Me\text{-}bpy)_2]^{2+}$ is redox inactive, with the reduction to Cu^I taking place at lower potential values ($E < -0.2$ V *vs* SCE).

DPV measurements on the benzyl-substituted Ni^{II} macrocyclic complex $[\mathbf{3b}]^{2+}$ disclosed a one-electron reversible process, in the oxidation scan, with a peak potential, E_p (which in this case equals $E_{1/2}$), of 795 mV *vs* SCE, corresponding to the oxidation of the Ni^{II} center to Ni^{III}. Ni^{II} tetraaza macrocyclic complexes typically undergo reversible one-electron oxidation processes to the Ni^{III} state, and, in particular, this value is consistent with the literature for the oxidation of Ni^{II} complexes with 14-membered tetraamine macrocyclic ligands having the same framework as cyclam. In particular, $[Ni^{II}(cyclam)]^{2+}$ is oxidized at $E_{1/2} = 740$ mV *vs* SCE (0.1 M NaClO₄ aqueous solution),[21] and it has been demonstrated that appending two or more methyl groups to the carbon atoms of the ligand backbone increases the oxidation potential[22] of the encircled Ni^{II} cation by 20−100 mV.

On addition of up to 5 equiv of NCO⁻, N₃⁻, and NCS⁻, the Ni^{II}/Ni^{III} potential was observed to decrease significantly. Such

(21) Buttafava, A.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Poli, G.; Seghi, B. *Inorg. Chem.* **1986**, *25*, 1456.
(22) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

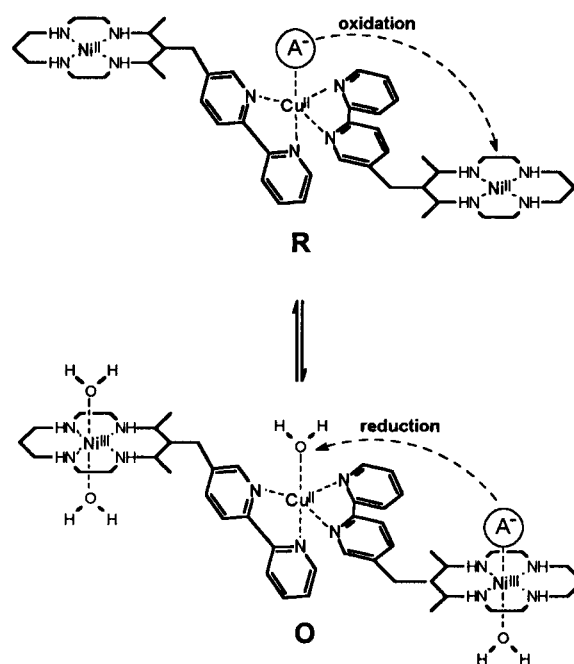**Figure 2.** Sketch of the electrochemically switched anion translocation process in the $[Cu^{II}(\mathbf{3a})_2(anion)]^{5+}$ system.

an effect was less pronounced in the case of Cl⁻ and was not observed at all for NO₃⁻. The potential shift toward less positive values has to be ascribed to the stabilization of the low-spin Ni^{III} state, which requires the metal to be six-coordinate, and benefits from the axial binding of the added anion.

DPV experiments under the same conditions (pulse width: 10 mV; scan rate: 2 mV s⁻¹) on the multicomponent species $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ produced a single peak with an E_p value of 805 mV *vs* SCE and with an half-peak width of 120 mV. This corresponds to the oxidation of the two Ni^{II} centers, exerting a moderate reciprocal electrostatic repulsion, and whose $E_{1/2}$ values are separated by 60 mV. Notice that the half-peak width ($W_{1/2}$) for two equivalent noninteracting sites is 90 mV, which corresponds to a separation between the $E_{1/2}$ values of 36 mV (the statistical term).[23] Spectrophotometric titration experiments (*vide supra*) have demonstrated that, in the case of N₃⁻, OCN⁻, and SCN⁻, the added anion is bound to the Cu^{II} center of the multicomponent system $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$ with a 1:1 stoichiometry. In particular, from the log K values obtained it is possible to calculate that when a 1:1 molar ratio of added anion is reached, with respect to Cu^{II} (i.e., molar ratio = 0.5 with respect to Ni^{II}), 97% (N₃⁻), 94% (NCO⁻), and 95% (NCS⁻) of the added anion is coordinated to Cu^{II}. In this sense, one can assume that up to 0.5 equiv, with respect to Ni^{II}, all of the anion that is added to the solution is *bound* to the copper center, corresponding to form **R** in Figure 2.

On this basis, one might expect that in an electrochemical titration experiment with NCO⁻, NCS⁻, and N₃⁻, the first 0.5 equiv (with respect to Ni^{II}) of the added anion should not greatly influence the potential values at which the oxidation of the two Ni^{II} centers takes place, as the Cu^{II} center makes the anionic species unavailable by *capturing* them from the solution.

On the contrary, it is found that on addition of the first 0.5 equiv (with respect to Ni^{II}), a steep, almost linear decrease of the Ni^{II}/Ni^{III} peak potential of the DPV profile is observed, with a variation at 0.5 equiv added, of −120, −155, and −120 mV for N₃⁻, NCO⁻, and NCS⁻, respectively. This indicates that the anion that is bound to the Cu^{II} center in $[Cu^{II}(\mathbf{3a})_2(H_2O)]^{6+}$

(23) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Table 1. E_p Values for Systems $[Cu(3a)_2(H_2O)]^{6+}$ and $[3b]^{2+}$ in Aqueous Solution (mV, *vs* SCE) in the Presence of Added Anions

$\dfrac{mol_{ad}\,_b}{mol_{Ni^{2+}}}$	$[Cu(3a)_2(H_2O)]^{6+}$, $E_p = 805^a$					$[3b]^{2+}$, $E_p = 795^{a,c}$				
	NCO^-	N_3^-	NCS^-	Cl^-	NO_3^-	NCO^-	N_3^-	NCS^-	Cl^-	NO_3^-
0.5	650	685	685	788	805	735	735	740	787	795
1.0	619	657	670	765	805	704	670	725	780	795
2.0	575	625	d	740	805	675	640	d	775	795
5.0	540	600		730	800	647	620		760	795

^{a} Counter anion = $CF_3SO_3^-$. ^{b} Where mol_{ad} = moles of added anion. ^{c} $E_p \equiv E_{1/2}$. ^{d} Further addition of NCS^- resulted in the precipitation of the complex.

(form **R** in Figure 2) stabilizes the oxidized $Ni^{III}Cu^{II}Ni^{III}$ state and *jumps* onto one of the peripheral Ni^{III} centers (form **O** in Figure 2). In addition, by comparing the decrease of the DPV peak potential after the addition of 0.5 equiv of anion for $[Cu^{II}$-$(3a)_2(H_2O)]^{6+}$ and $[3b]^{2+}$ (see Table 1), it can be seen that in the case of the multicomponent species $[Cu^{II}(3a)_2(H_2O)]^{6+}$, the E_p decrease is much higher than that found for the benzyl-substituted component $[3b]^{2+}$. Thus, by fixing the anions added to the Cu^{II} center, the oxidized $Ni^{III}Cu^{II}Ni^{III}$ species gain an extra stabilization (ranging from 60 to 90 mV), due to the favorable position of the anion that goes on the Ni^{III} center; rather than from the bulk of the solution, the electrochemically generated Ni^{III} centers can take the anion from a proximate, fixed position, with the effective anion concentration, thus, being hugely increased (in a broader sense, this situation may recall the chelate effect, as interpreted by Schwarzenbach).[24]

This behavior demonstrates the intramolecular nature of the anion transfer and excludes the occurrence of any intermolecular reaction: the redox equilibrium between the $[Cu^{II}(3a)_2(A)]^{5+}$ complex (A = N_3^-, NCO^-, NCS^-) and its doubly oxidized form can be thus represented as in Figure 2. The envisaged anion is translocated from the center (form **R**) to the periphery (form **O**) of the system by varying the redox potential, i.e., by switching the oxidation state (II to III) of the peripheral metal cations.

Comparison of the electrochemical titration profiles for $[Cu^{II}$-$(3a)_2(H_2O)]^{6+}$ and $[3b]^{2+}$ with the anions over the whole range of molar ratios studied, gives visual evidence of the phenomenon discussed. As an example, the E_p *vs* mol of NCO^-/mol of Ni^{II} profile is reported in Figure 3.

The starting oxidation potentials (no anion added, $NaCF_3$-SO_3 as the background electrolyte) are the same for the two species, but during the addition of the first 0.5 equiv of NCO^-, the E_p value of $[Cu^{II}(3a)_2(H_2O)]^{6+}$ decreases much more steeply than that of $[3b]^{2+}$. From 0.5 equiv on, all of the added NCO^- goes into the bulk solution in the case of $[Cu^{II}(3a)_2(H_2O)]^{6+}$. According to this, the Ni^{II}/Ni^{III} oxidation potential further decreases, but with a less steep profile, which parallels that of $[3b]^{2+}$. However, it must be noted that even in the presence of a large excess of NCO^-, the advantage gained by $[Cu^{II}(3a)_2$-$(H_2O)]^{6+}$ from the first 0.5 equiv is still maintained.

Finally, the cases of NO_3^- and Cl^- must be taken into consideration. The nitrate anion is not able to stabilize the Ni^{III} state in complexes with tetramino macrocyclic ligands, probably due to its relatively poor affinity toward the Ni^{3+} cation. As a matter of fact, even with a 5-fold excess of nitrate, the E_p of the $[Cu^{II}(3a)_2(H_2O)]^{6+}$ and $[3b]^{2+}$ species does not vary. On the other hand, addition of the chloride anion affects the redox potential of $[3b]^{2+}$ ($\Delta E_p \approx -10$ mV at 0.5 equiv). This is in

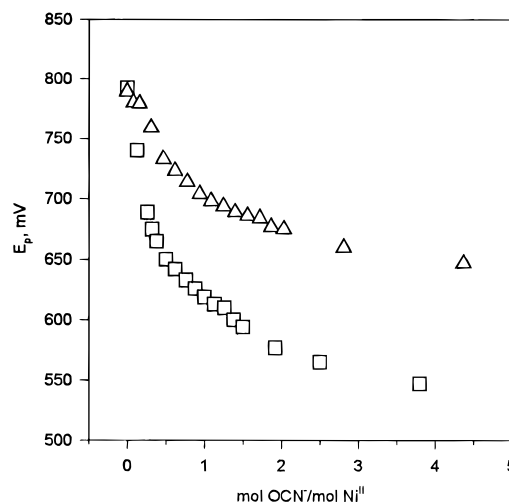**Figure 3.** Electrochemical titration profiles (E_p *vs* mol of anion/mol of Ni^{II}) with OCN^-, in the case of $[Cu^{II}(3a)_2(H_2O)]^{6+}$ ($\square$) and $[3b]^{2+}$ ($\triangle$). For the species $[3b]^{2+}$, $E_p \equiv E_{1/2}$.

good agreement with what has already been found for other tetraamino macrocyclic complexes containing nickel in aqueous solution:[25] the moderately coordinating Cl^- anion exerts a slight stabilization effect on the Ni^{III} species. On passing to the multicomponent system $[Cu^{II}(3a)_2(H_2O)]^{6+}$, no striking differences are found (see Table 1); also in this case, a very moderate decrease of the Ni^{II}/Ni^{III} oxidation potential is observed. This is in accord with what was found for the spectrophotometric titration experiments: the chloride anion binds the Cu^{II} center of $[Cu^{II}(3a)_2(H_2O)]^{6+}$ with a very low equilibrium constant (log $K \ll 2$), so that only a fraction of the added Cl^- goes on the Cu^{II} center, the larger part remaining in the bulk of the solution. Thus, the Ni^{III} cation which forms cannot be stabilized by taking an easily available anion from the proximal Cu^{II} "stepping stone".

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