

Controlled Molecular Motions in Copper-Complexed Rotaxanes: An XAS Study

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The environment of the central metal of a molecular machine-like copper rotaxane was observed by XAS experiments. The wheel of the rotaxane is a hetero-bischelating macrocycle containing both bidentate (phenanthroline) and terdentate (terpyridine) moieties. The axle of the assembly contains only a bidentate moiety. Applying an external chemical stimulus—oxidation of the metal—increases the number of coordinating atoms required by the metal template from 4 to 5. This variation is consistent with the oscillation of the wheel around the axle, leading thus to the most stable environment for the metal in the Cu(II) rotaxane.

Introduction

Molecular motors of various kinds are very common in biology.¹ By contrast, artificial motors at the molecular level have been less well-known until recently. Molecular motors can be defined as molecular assemblies in which some parts can be set in motion by an external signal, such as proton, electron, or photon transfer, while other parts remain motionless. The energy introduced by external stimulation allows the systems to undergo some kind of continuous motion.

The development of artificial systems² is a field which is currently being intensively explored. In particular, interest is being focused on transition-metal-containing systems,^{3–22} some

of which are based on the different stereochemical requirements of the various oxidation states of a metal.²³

The route developed by our group is based on copper complexes. Cu(I) is generally low-coordinate (coordination number ≤ 4) whereas Cu(II) exhibits preferentially square planar or higher coordination (coordination number = 5 or 6). Upon reduction or oxidation of the copper center, from a situation corresponding to a stable complex, the system is set out of equilibrium. The relaxation process of the compound requires a large-amplitude motion to bring the system to its new equilibrium position.

Ligands such as catenanes and rotaxanes, in which the constituents of the multicomponent system are mechanically linked, are well suited in this context. Catenanes are compounds consisting of interlocked macrocycles. Rotaxanes are composed of one or more macrocycle(s) encircling a single-dumbbell component which bears a large blocking group or stopper at each end of the linear thread. In such molecules, relative motions of the molecular components—rotation, translation, ...—can be reversibly manipulated.

In the first of such systems described by our group—combining interlocked or threaded ligands with copper metal centers—gliding of one ring within the other in a two-copper catenane could be electrochemically or photochemically triggered.^{22,24} On the basis of the same principle, translation of a ring along an axle in a copper rotaxane was demonstrated.²³ More recently, oscillation of a ring around an axle was described²⁵ and the rate constants for each of the sequential steps

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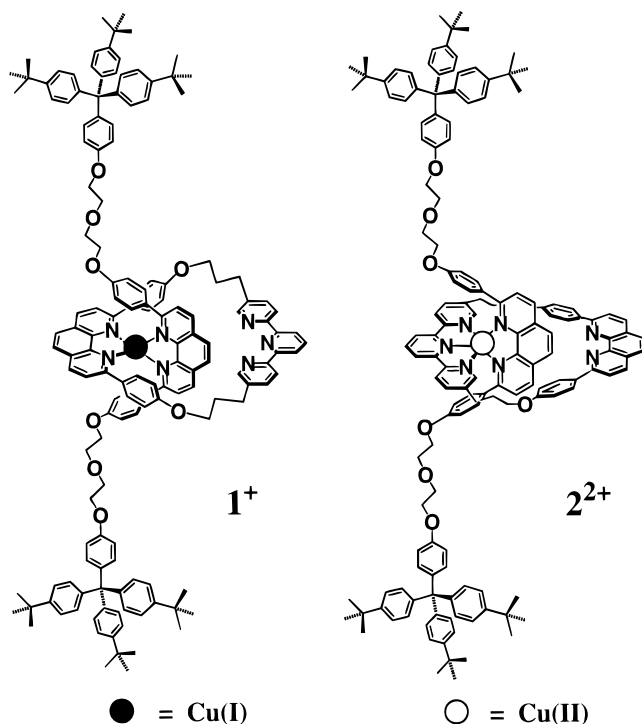


Figure 1. Copper(I) rotaxane 1^+ (4-coordinate form) and copper(II) rotaxane 2^{2+} (5-coordinate form).

were determined using electrochemical techniques. In this system (Figure 1), the metal ion can be coordinated either by two bidentate units or by one bidentate and one terdentate ligand. Upon variation of the redox state of the metal ($\text{Cu}^{\text{I}} \leftrightarrow \text{Cu}^{\text{II}}$), the geometry around the copper will switch from a tetrahedral arrangement (two bidentate units) to a 5-coordinate one (one terdentate and one bidentate).

Since the redox potential values for the pentacoordinated^{22,24} $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple and for the tetracoordinated^{26,27} $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple are different, it was thus possible to determine the number of donor atoms around the metal. In addition, the interconversion between the two states (coordinations 4 and 5) could be monitored, this event corresponding to a relaxation process following the perturbation signal (change of the metal oxidation state).

XAS techniques are well suited for observing the environment of metals. We will show here how these techniques offer evidence of the modification of the coordination sphere of copper on changing its redox state from (I) to (II). This modification is the consequence of the large-amplitude motion of one constituent of the molecular assembly with respect to the other. EXAFS is thus a powerful tool for following such externally triggered motions inside metal-containing molecular systems.

Experimental Section

The syntheses of rotaxanes 1^+ and 2^{2+} ²⁵ and reference compounds $\text{Cu}^{\text{I}}(\text{dap})_2(\text{BF}_4)$ and $\text{Cu}^{\text{II}}(\text{dap})_2(\text{BF}_4)_2$ ²⁶ are described elsewhere (dap = 2,9-dianisyl-1,10-phenanthroline).

Sample Preparation. For reference compounds, 5×10^{-4} mol L^{-1} solutions of $\text{Cu}^{\text{I}}(\text{dap})_2(\text{BF}_4)$ and $\text{Cu}^{\text{II}}(\text{dap})_2(\text{BF}_4)_2$ in acetonitrile were prepared. For rotaxane 1^+ , a 5×10^{-4} mol L^{-1} solution in a 7/3 (v/v) mixture of acetonitrile and dichloromethane was prepared. Rotaxane

2^{2+} was prepared in situ, by adding a titrated solution of bromine in CH_2Cl_2 (10^{-2} mol L^{-1}). Addition of this oxidant was followed by a change in color of the rotaxane solution, which immediately turned from red to green.

XAS Measurements. XANES and EXAFS experiments were recorded at the European Synchrotron Research Facility (ESRF, Grenoble, France) on the ID26 beamline, equipped with a monochromator having a pair of Si(220) crystals.

For the recording of solution spectra, a Teflon cell with Kapton windows was used. All the samples were studied at the Cu K-edge from 8830 to 9650 eV using the quick-EXAFS technique in the fluorescence mode (measured with silicon PIN diodes) at room temperature. The technical developments needed to perform quick-EXAFS and the technical characteristics of the ESRF ID26 beamline have been exhaustively described elsewhere.^{28,29} The X-ray absorption spectra were converted to an energy scale using a copper foil as the internal standard, with the energy of the maximum of the spectral derivative of the copper foil defined at 8979 eV.

Data Analysis. The analysis was performed by employing a harmonic approximation with plane waves³⁰ using a program developed by Aberdam.³¹ The procedure used for data analysis has been extensively described in a previous paper.³²

Results and Discussion

Transition-Metal-Containing Rotaxanes. The systems studied here are rotaxanes 1^+ and 2^{2+} . The molecular components are the same for both compounds. They differ in the redox states of the metal, Cu(I) for 1^+ and Cu(II) for 2^{2+} , and in the environments of the metal centers.

The axle of the rotaxane consists of a molecular thread in which a 2,9-diphenyl-1,10-phenanthroline (dpp) core, a bidentate binding domain, is linked via a diethoxy ether spacer to two bulky ancillary tetraaryl substituents,³³ which act as stoppers. The wheel is a hetero-bis-chelating macrocycle,²² including a bidentate unit, here again a diphenylphenanthroline moiety, and a terdentate unit, a 2,2':6',2''-terpyridine moiety. Rotaxane 1^+ was obtained using the powerful template effect^{34–36} of Cu(I); threading the monostoppered axle through the macrocycle was followed by grafting the second stopper onto the other end of the thread. This synthesis has been described previously.²⁵ Rotaxane 2^{2+} could be obtained either by demetalation³⁷ of 1^+ and remetalation with Cu(II) ions or by chemical or electrochemical oxidation of rotaxane 1^+ .

Electrochemically Induced Pirouetting of the Ring on the Threaded Dumbbell. 2,9-Diphenyl-1,10-phenanthroline derivatives strongly stabilize the lower oxidation state of copper, Cu(I), leading to entwined complexes in which the metal is in a tetrahedral environment.³⁸ Thus, in rotaxane 1^+ (Figures 1

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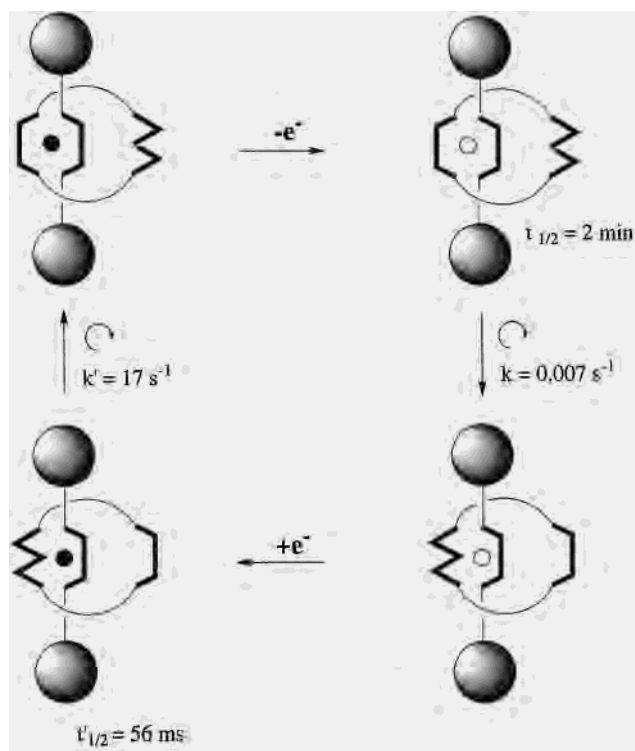


Figure 2. Principle of the electrochemically induced molecular motions in a copper rotaxane complex. The stable 4-coordinate monovalent complex is oxidized to an intermediate tetrahedral divalent species. This compound undergoes a rearrangement to afford the stable 5-coordinate copper(II) complex. Upon reduction, the 5-coordinate monovalent state is formed as a transient species. Finally, the latter undergoes a reorganization process that regenerates the starting complex (the filled circle represents Cu^I, and the open circle represents Cu^{II}). k and k' are the rate constants of these two reorganization processes. $t_{1/2}$ and $t'_{1/2}$ are the half-lives of the tetracoordinate species and the pentacoordinate monovalent species, respectively.

and 2), the metal is coordinated by the dpp unit of the thread and the dpp subunit of the hetero-bis chelating macrocycle. This was clearly shown by ¹H NMR and UV-vis spectroscopic measurements.²⁵

Since copper(II) preferentially coordinates five donor atoms (Figures 1 and 2), the metal in rotaxane **2**²⁺ is coordinated to the dpp unit of the thread and to the terpyridine subunit of the macrocycle when the system is in equilibrium.

Oxidizing the metal center in rotaxane **1**⁺ (Figure 2), in which the copper is tetracoordinated, leads to a transient tetracoordinated copper(II) rotaxane. This compound undergoes a rearrangement, which leads to the stable 5-coordinate copper(II) complex, rotaxane **2**²⁺. The reverse procedure, an electron transfer onto rotaxane **2**²⁺, leads to a pentacoordinated copper(I) rotaxane. Here again, a reorganization of the coordination sphere, by the pirouetting of the macrocycle around the dumbbell, leads to the most stable conformation for the reduced metal, i.e., rotaxane **1**⁺.

The redox potentials of rotaxanes **1**⁺ and **2**²⁺ are the thermodynamic expressions of the relative stabilities of tetracoordinated Cu(I) vs tetracoordinated Cu(II) and of pentacoordinated Cu(II) vs pentacoordinated Cu(I). Thus, for rotaxane **1**⁺, the redox potential for the Cu^{II}/Cu^I couple reaches 0.6 V vs SCE (Figure 3a), whereas stabilization of Cu(II) in rotaxane **2**²⁺ displaces the redox potential cathodically by 700 mV (in rotaxane **2**²⁺, $E(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) = -0.1 \text{ V}$ vs SCE; Figure 3b).

The rate constants for the reorganization processes around 5-coordinate Cu(I) and 4-coordinate Cu(II) are markedly different. Their values have been determined by electrochemical

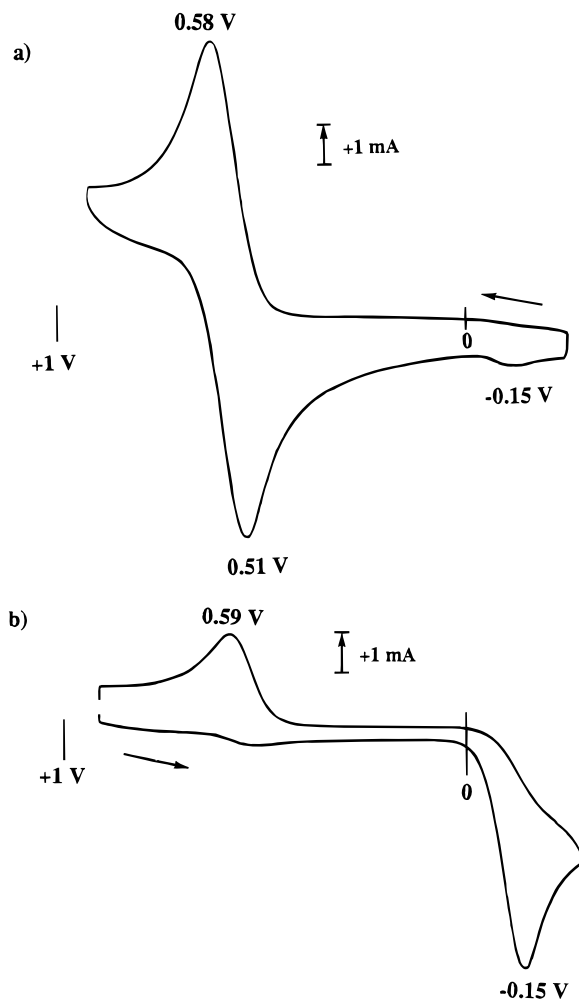


Figure 3. Cyclic voltammograms recorded using a Pt working electrode at a 100 mV s^{-1} sweep rate [$\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (4/1 v/v); supporting electrolyte tetrabutylammonium tetrafluoroborate, 0.1 mol L^{-1} ; Ag wire pseudoreference]: (a) copper(I) rotaxane **1**⁺; (b) copper(II) rotaxane **2**²⁺.

techniques²⁵ and are indicated in Figure 2. The rearrangement around Cu(I) is 2500 times faster than that around Cu(II). This large difference is underlined by the irreversibility of the reduction wave of rotaxane **2**²⁺, combined with the appearance, during the reverse scan, of the characteristic oxidation peak of tetracoordinated Cu(I), at $+0.6 \text{ V}$, which indicates that the rearrangement around pentacoordinated Cu(I) is a fast process. On the other hand, the perfect reversibility of the oxidation of rotaxane **1**⁺ (even at a slow potential rate) stresses the pronounced difference between the rate constants for the reorganization processes around pentacoordinated Cu(I) and tetracoordinated Cu(II).

X-ray Absorption Spectroscopy (XAS) Measurements. X-ray absorption spectroscopy³⁹ allows the determination of the close environment of a metal. In the case of the systems described here, this technique is a powerful tool for observing the coordination sphere of the copper(I) or -(II) center. Moreover, correlation of these spectroscopic techniques with the electrochemical characteristics of rotaxane **1**⁺ and **2**²⁺, which are the two most stable molecular conformations thermodynamically, should permit the difference in coordination number to be confirmed.

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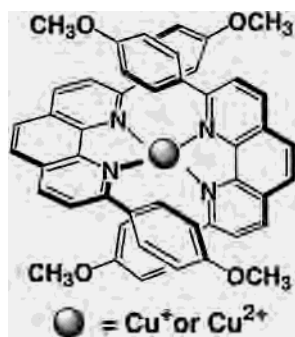


Figure 4. Bis(2,9-di-*p*-anisyl-1,10-phenanthroline)copper(I) or -copper(II).

The structures of two compounds were used as references (Figure 4), $\text{Cu}^{\text{I}}(\text{dap})_2(\text{BF}_4)$ and $\text{Cu}^{\text{II}}(\text{dap})_2(\text{BF}_4)_2$.

The spectrum of $\text{Cu}^{\text{I}}(\text{dap})_2^+$ was thus compared to that of rotaxane $\mathbf{1}^+$, for which a similar environment was expected for the metal. The crystal structures of $\text{Cu}^{\text{I}}(\text{dap})_2^+$ and the analogue $\text{Cu}^{\text{I}}(\text{dpp})_2^+$ are known. The coordination geometry for the copper(I) center in $\text{Cu}^{\text{I}}(\text{dap})_2^+$ (Cu–N bond distances: 2.053 and 2.067 Å)⁴⁰ and in $\text{Cu}^{\text{I}}(\text{dpp})_2^+$ (Cu–N bond distances: 2.019 and 2.11 Å for one dpp, 2.032 and 2.082 Å for the other)⁴¹ is best described as distorted and dissymmetrical tetrahedral. Concerning the Cu(II) oxidation state, only the crystal structure of $\text{Cu}^{\text{II}}(\text{dpp})_2^{2+}$ was used, since that of $\text{Cu}^{\text{II}}(\text{dap})_2^{2+}$ was not available. The coordination geometry for the copper(II) center in $\text{Cu}(\text{dpp})_2^{2+}$ (Cu–N bonds between 1.98 and 1.997 Å)⁴¹ is best described as flattened tetrahedral, with no additional ligand, which is quite unusual for copper(II) bis(diimine) complexes. In the case of the Cu(II) rotaxane $\mathbf{2}^{2+}$, it was expected that the XAS spectra would be dramatically different from those of $\text{Cu}^{\text{II}}(\text{dpp})_2^{2+}$ if the metal in $\mathbf{2}^{2+}$ is indeed pentacoordinated.

The shapes of XANES spectra are very sensitive to the electronic structure and to the geometry around the copper ion.^{42,43} This region corresponds to forbidden $1s \rightarrow 3d$ and allowed $1s \rightarrow 4p$ transitions of the excited photoelectron to

vacant bound states of *p*-symmetry, and the ordering of these vacant orbitals is dependent on the geometry of the coordination sphere. Therefore, a qualitative comparative XANES study between reference compounds and rotaxanes $\mathbf{1}^+$ and $\mathbf{2}^{2+}$ was undertaken before EXAFS analysis.

For $\text{Cu}^{\text{I}}(\text{dap})_2(\text{BF}_4)$, the spectrum displays a first strong transition (prepeak transition) at 8985 eV and then the white line at 8995 eV and a shoulder at 9005 eV. These two successive transitions result from the well-known distortion⁴¹ of the tetrahedral environment for this Cu(I) complex: this leads to a split of the 4*p* orbitals.⁴² Therefore, the two successive transitions have been assigned to $1s \rightarrow 4p_z$ and $1s \rightarrow 4p_{xy}$, respectively.⁴⁴ The similarity of the XANES spectra of rotaxane $\mathbf{1}^+$ and $\text{Cu}^{\text{I}}(\text{dap})_2(\text{BF}_4)$, illustrated in Figure 5, confirms that, in rotaxane $\mathbf{1}^+$, the geometry around the metal can once again be described as distorted and dissymmetrical tetrahedral. This means that, in the most stable conformation of the reduced state of the metal rotaxane, the copper(I) atom is coordinated to the dpp unit of the molecular thread and to the dpp fragment of the macrocycle.

Concerning $\text{Cu}^{\text{II}}(\text{dap})_2(\text{BF}_4)_2$, the XANES spectrum (Figure 5) displays a shift in the edge energy of +2 eV compared to the Cu(I) reference spectrum. A shoulder at 8988 eV is followed by two main peaks at 8995 and 9002 eV. The spectrum of rotaxane $\mathbf{2}^{2+}$ is markedly different from that of $\text{Cu}(\text{dap})_2^{2+}$. The intensity of the white line at 9000 eV is higher than those for the two reference compounds, both of which have a coordination number of 4. This suggests that, for $\mathbf{2}^{2+}$, the coordination number is probably different.

The structural parameters deduced from the analysis of the EXAFS spectra are summarized in Table 1. In a previous paper, analysis of the EXAFS spectrum of the reference complex [$\text{Cu}(\text{dap})_2$]⁺ demonstrated that a Fourier-filtered first shell gives the best fit with four nitrogen atoms as the closest neighbors. The optimized average bond length is 2.035 Å, with a relatively broad distribution of distances, as suggested by the rather high value of the Debye–Waller factor ($s^2 = 7.1 \times 10^{-3} \text{ \AA}^2$). All

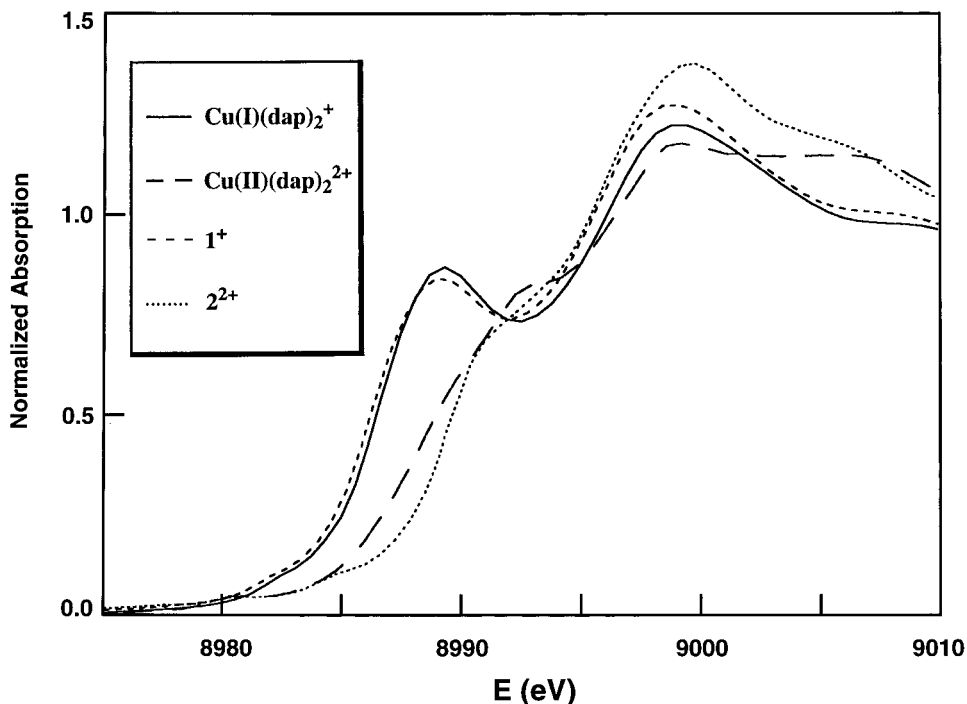


Figure 5. XANES spectra of the reference complexes bis(2,9-di-*p*-anisyl-1,10-phenanthroline)copper(I) and -copper(II) and of copper rotaxanes $\mathbf{1}^+$ and $\mathbf{2}^{2+}$.

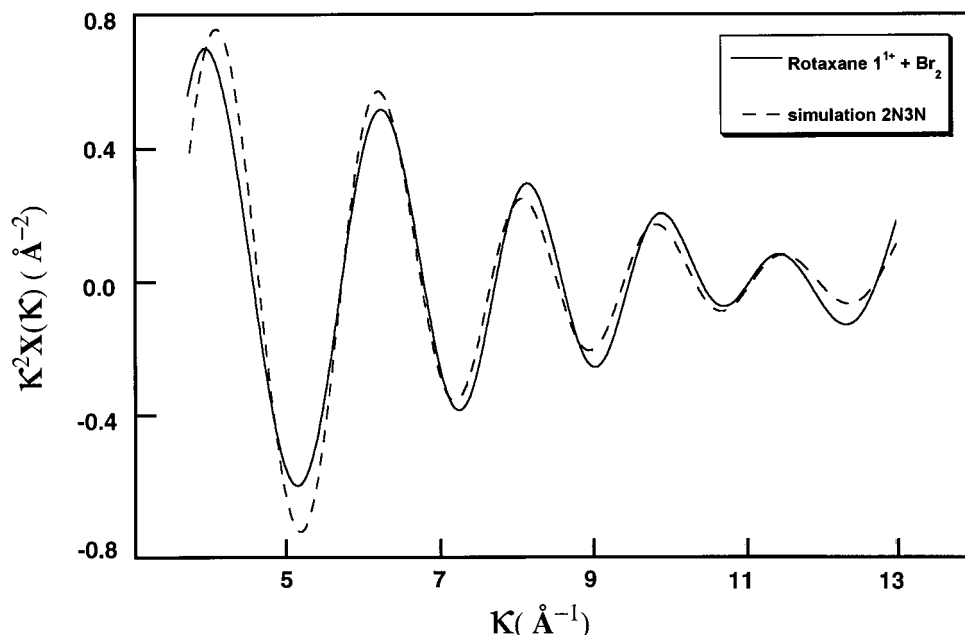


Figure 6. Fourier-filtered first shell of 2^{2+} prepared by oxidation of 1^+ with Br_2 and corresponding best fit for a 2N–3N environment.

Table 1. Cu–N Distances for the Fits of the Reference Complexes Bis(2,9-di-*p*-anisyl)-1,10-phenanthroline)copper(I) and -copper(II) and of Copper Rotaxanes 1^{1+} and 2^{2+}

	no. of nitrogens in shell	Cu–N (Å)	σ^2 (10^{-3}Å^2)
$\text{Cu}^{\text{I}}(\text{dap})_2^+$	4	2.035 ± 0.002	7.1 ± 0.5
$\text{Cu}^{\text{II}}(\text{dap})_2^{2+}$	4	2.011 ± 0.001	4.6 ± 0.2
$1^{1+ a}$	4	2.037 ± 0.002	5.8 ± 0.2
$2^{2+ b}$	3	1.985 ± 0.003	4.3 ± 0.4
	2	2.104 ± 0.003	0.87 ± 0.4

^a $\Delta E = 0$ eV. ^b $\Delta E = 2$ eV.

attempts to discriminate between the different nitrogen atoms led to worsening fits.

EXAFS studies on the copper(I) rotaxane 1^+ show that four nitrogen atoms can be identified as the nearest neighbors, at distances of 2.037Å from the metal, which is very close to the value obtained in the case of $[\text{Cu}(\text{dap})_2]^+$ (2.035Å). This observation confirms XANES analyses. But, for the rotaxane, the Debye–Waller factor is smaller, indicating a fairly narrow distance distribution.

For the copper(II) rotaxane 2^{2+} , simulations with one shell of four or five nitrogen donors led only to very bad fits with no physical parameters. The best simulation found, Figure 6, was obtained with a five-nitrogen environment split into two 2N–3N subshells (Table 1). The first one contains three nitrogens with a Cu–N average distance of 1.985Å . The two nitrogens of the second shell are at distances of 2.104Å from the metal.

These results are well matched with a coordination sphere formed of one phenanthroline and one terpyridine (Figure 7). Indeed, in this configuration, it can be assumed that the external

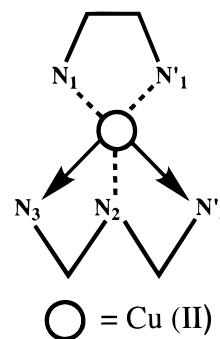


Figure 7. Schematic representation of the coordination sphere of the metal center in copper(II) rotaxane 2^{2+} . N1 and N'1 refer to the nitrogen atoms of the phenanthroline core; N2, N3, and N'3 refer to those of the terpyridine unit. One coordinating subshell includes atoms N1, N'1, and N2; the second contains the two external nitrogen atoms of the terpyridine subunit, N3 and N'3 (see text).

nitrogen atoms from the terpyridine, N3 and N'3, are quite remote and nearly equidistant from the metal center. This last point explains the small value of the Debye–Waller factor (Table 1) for this subshell. The first shell includes the three atoms nearest the copper, which are the two nitrogen atoms of the phenanthroline (N1, N'1) and the central nitrogen of the terpyridine (N2, Figure 7). Cu–N1 and Cu–N'1 distances can be assumed to be relatively similar but different from the Cu–N2 distance. This explains the high σ^2 value found for this shell. These nitrogen–copper(II) distances deduced from EXAFS measurements are close to those determined by X-ray studies on terpyridine- and dpp-containing copper(II) complexes. In $\text{Cu}^{\text{II}}(\text{terpy})_2(\text{PF}_6)_2$ crystals, distances of 1.977 and 2.179Å were found for Cu(II)–N2 and Cu(II)–N3(N'3) bonds, respectively.⁴⁵ By EXAFS measurements, lengths of 1.985 and 2.104Å were assigned to Cu(II)–N2 and Cu(II)–N3(N'3) bonds in 2^{2+} . Likewise, the average of the distances between copper and N1, N'1, and N2 (1.985Å ; EXAFS study) lies in the same range as the Cu–N distances in $\text{Cu}^{\text{II}}(\text{dpp})_2(\text{ClO}_4)_2$ crystals (1.980 – 1.997Å ; X-ray study).⁴¹

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The copper rotaxane described here exists in two totally different conformations, depending on the redox state of the metal. Whereas the external orbitals of the metal take part in electron transfer reactions, only the deep electrons (of the metal) are involved during XAS experiments. Electrochemical measurements demonstrated that the oxidation of the copper(I) rotaxane $\mathbf{1}^+$ leads to a copper(II) rotaxane with a formal redox potential which is dramatically different from that of $\mathbf{1}^+$. This was explained by the change of the ligands around the metal following the electron transfer step. This reorganization of the coordination sphere can only be achieved by the pirouetting of the hetero-bischelating macrocycle around the monochelating molecular thread.

XAS studies, which are described here, showed that, in its lower oxidation state, the metal is surrounded by four nitrogen atoms, which are assumed to be the two phenanthroline cores from the ligands: macrocycle and thread. After oxidation of the metal, XAS showed that the metal is surrounded by five nitrogen atoms. This 2N–3N shell is consistent with the coordination of one phenanthroline and one terpyridine to the metal. Here again, only a half-turn of the wheel around its axle can lead to such a modification of the environment of the metal.

Conclusion

The pirouetting of a wheel around its axle in a copper-containing rotaxane following a redox stimulus has been

demonstrated by XAS experiments. It could be observed, by these techniques, that the environments about the metal centers are different in the stable conformations of reduced and oxidized states. Whereas XANES and EXAFS observations are in agreement with a distorted arrangement of the tetrahedron formed by the coordinating nitrogens for copper(I) rotaxanes, these spectroscopic measurements lead to the conclusion that, in copper(II) rotaxanes, the 5-ligand coordination sphere can be described by two subshells. The one nearest the metal contains three nitrogen atoms, one being attributed to the terpyridine moiety of the macrocycle and the two others to the phenanthroline unit of the molecular thread. The second subshell includes the two external coordinating atoms of the terdentate core. These totally different environments for the metals in going from Cu(I) to Cu(II) oxidation states correlate with the different formal redox potentials for Cu(I) and Cu(II) rotaxanes when they are in their most stable conformations and are explained by the pirouetting of the hetero-bischelating macrocycle around its axle upon changing the redox state of the metal.

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