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Copper(II/I) Complexes of a Hexakis(bipyridyl)cyclotriveratrylene Ligand: A Redox-Induced Conformational Switch

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A series of copper(II) and copper(I) complexes have been synthesized with ligands combining 6-methyl-2,2′-bipyridines with cyclotriveratrylene (CTV) (**1**) and with catechol (**2**). The electrochemical, ^{1}H NMR, and mass spectrometry characterizations of these complexes are described and discussed. The six pendant bipyridines of ligand **1** allow for the formation of two trinuclear copper(I) complexes $[(\mathbf{1})Cu_3](BF_4)_3$ differing only in the conformation "vic" or "int" adopted by the ligand to fit the tetrahedral cuprous ions. Similarly, **1** generates two trinuclear copper(II) complexes in which the conformation of the ligand fits the square planar geometry of cupric ions. In both the cuprous and cupric complexes, a conformational equilibrium exists. Ligand **2** bearing two methylbipyridines has proven to be a useful model of the coordinating sites of ligand **1**. In this case, two homologous copper(I) complexes are obtained, $[(\mathbf{2})Cu]BF_4$ and $[(\mathbf{2})_2Cu_2](BF_4)_2$, modeling respectively two possible coordination conformations of ligand **1**. With copper(II), ligand **2** yields only one complex $[(\mathbf{2})Cu](CF_3SO_3)_2$, which allows for the unambiguous identification of the conformations observed for ligand **1** complexes. The different coordinating modes of ligand **1** in the complexes mentioned are in exchange but exhibit different physical properties, thus representing a new bistable system based on conformational isomerism which exhibits an electrochemical potential hysteresis. An equilibrium constant and thermodynamic data were obtained for this system by variable-temperature cyclic voltammetry. The influence of coordinating vs noncoordinating solvents was also studied.

Introduction

For the past 20 years, 2,2′-bipyridine (bipy) has probably been among the most studied ligands in coordination chemistry, owing to its ability to complex a wide range of metals, from alkali to transition and rare earth metals.[1] Frequently combined with polyether chains[2−5] or amines,[5−11] bipy has also been exhaustively introduced in macrocyclic structures, combining the properties of the metal complexes with the stabilizing features of macrocyclic ligands. During the course of this work, several groups have reported the introduction of bipyridyl groups on calix[4]arene moieties, as well as the coordinating properties of these ligands with regard to transition metals and rare earth cations.[12−14] The interest of the metallic complexes obtained varies from particular photochemical, electrochemical,[5−7,10] or allosteric[2] properties to the recent processes of self-assembly around metallic templates, for example the spontaneous formation of helicates with bipy-containing strands.[15−20] Although several uses of cyclotriveratrylene (CTV) as a complexing unit for lipophillic substrates have been described in the literature,[21] only a few metal complexes taking advantage of the CTV framework have been reported so far.[22−24] Following the synthesis of a CTV derivative **1** bearing six pendant bipyridyl groups,[25] this paper describes the complexation studies and the preparation of the copper(II/I) complexes with ligand **1**. The properties of these complexes will also be discussed. Due to

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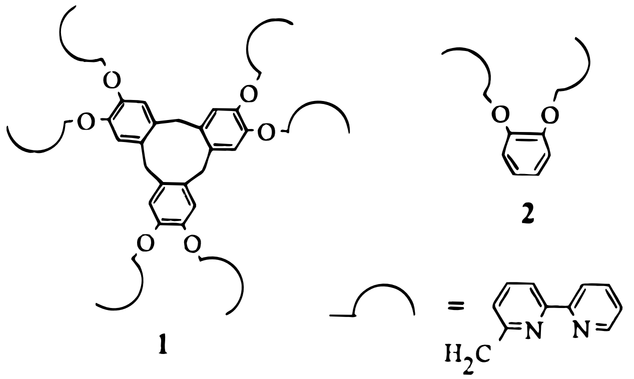

Figure 1. Ligands studied: **1** allows for trinuclear square planar or tetrahedral complex formation; **2** is a simpler model of the chelating site involved in metal complexation with **1**.

the arrangement of the bipy groups around CTV's rigid matrix, ligand **1** depicted in Figure 1 was expected to form trinuclear tetrahedral or square planar complexes. For comparative studies, a fragment **2** (Figure 1) of a possible coordinating subunit has been synthesized and its properties have been compared to those measured for **1**. The synthesis of ligand **2** was performed by simple reaction of an excess of 6-(bromomethyl)-2,2′-bipyridine with catechol in the presence of potassium carbonate in dimethylformamide.

Cuprous and cupric complexes were obtained on preparative scale by stoichiometric reactions of ligands **1** and **2** with either $Cu(CH_3CN)_4BF_4$ or $Cu(CF_3SO_3)_2$. The stoichiometry of the complexes with ligand **1** has been determined both by UV-visible and by electrochemical methods. The nature of ligands **1** and **2** offers several possible arrangements of the bipyridine subunits around the metallic centers, for both copper(I) and copper(II), as depicted in Figure 2.

For copper(I) complexes of ligand **1**, the metal cations may be coordinated by two bipyridines situated on the same catechol subunit or by two bipyridines attached to neighboring catechol subunits. The former coordination mode will be referred to as internal (int) while the latter will be called vicinal (vic). Each trimetallic copper(I) complex is composed of three helices which may be λ or δ oriented. Thus, two enantiomeric and two mesomeric complexes may be formed for both the "int" and the "vic" coordination modes. These eight different isomers are shown in Figure 2a,b. In contrast, only two isomers, "vic" or "int" are expected for square planar copper(II) complexes of **1** (Figure 2c).

With ligand **2** and copper(I), monomeric and dimeric complexes may be formed (Figure 2d). The helix formed in the mononuclear complex may be λ or δ oriented, and no mesomers are possible. For dimeric compounds, composed of two metal cations and two ligand **2** moieties, two enantiomers (helicates) and one mesomer (face to face) are possible. Only one mononuclear copper(II) complex can be envisioned with ligand **2** (Figure 2d).

Experimentally, only a few of the different possible isomers are observed for each type of compound. As described in this paper, the combination of ^1H NMR, mass spectrometry, and electrochemical methods allows for the distinction between the different possible isomers obtained.

Experimental Section

General Experimental Conditions. Electrochemical measurements were performed in 0.1 M solutions of tetra-*n*-butylammonium hexafluorophosphate ($(TBA)PF_6$, commercial grade, Fluka) in dry *N*,*N*-dimethylformamide (DMF) or methylene chloride (CH_2Cl_2). DMF was purified according to ref 26, and CH_2Cl_2 (Carlo Erba) was dried on 4 Å molecular sieves. The synthesis of CTV(bipy)$_6$ (**1**) has been previously reported.[25] Copper complexes prepared in situ were obtained by addition of copper(II) triflate, $Cu(CF_3SO_3)_2$, or copper(I) tetrakis(acetonitrile) tetrafluoroborate, $Cu(CH_3CN)_4BF_4$, to a ligand solution containing 0.1 M $(TBA)PF_6$. Polarographic measurements were performed in 0.1 M $(TBA)PF_6$ solutions in DMF on a PRG4 (SOLEA-TACUSSEL) apparatus, with a classical three-electrode setup: mercury drop as working electrode (WE), platinum wire as counter electrode

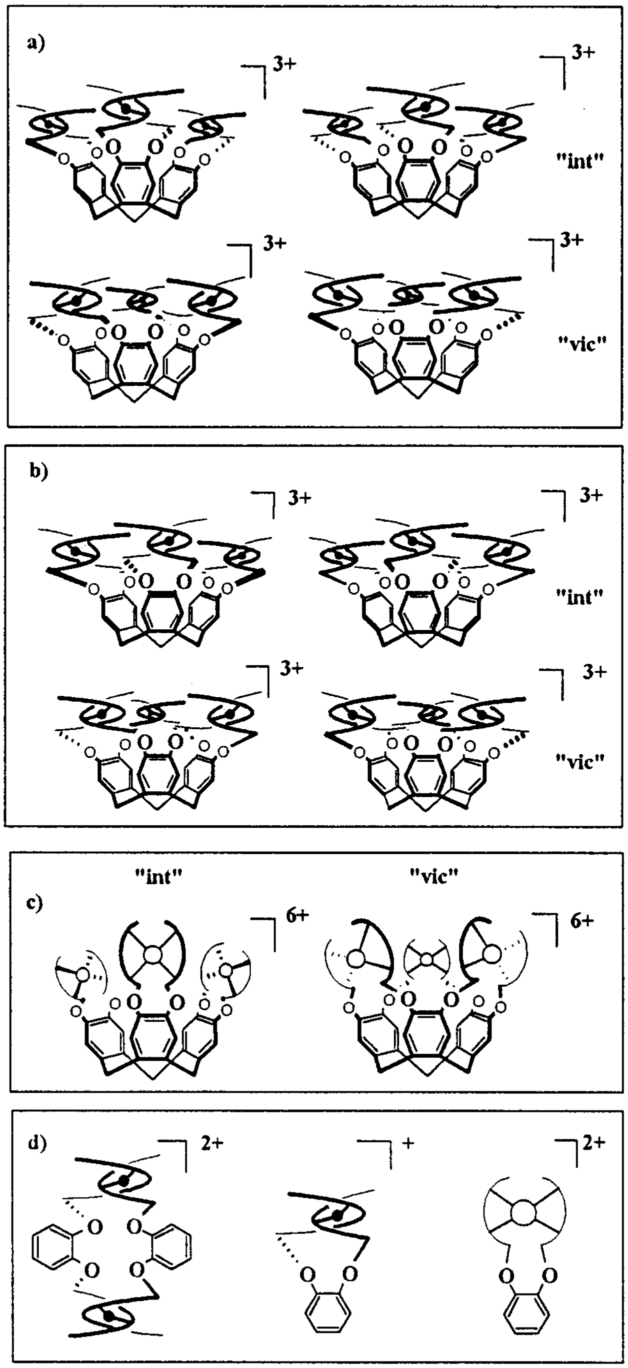

Figure 2. Possible coordination modes of copper(II) (white circle) and copper(I) (black circle) with **1** and **2**: (a) enantiomeric forms of copper(I) complexes; (b) corresponding mesomeric forms; (c) conformers of copper(II) complexes; (d) model complexes of **2** with copper(II) and copper(I). The same symbolism will be used throughout this paper: (i) coordinating bipyridines located on the same catechol noted "int"; (ii) coordinating bipyridines located on distinct catechols noted "vic".

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(CE), and saturated calomel electrode (0.1 M (TBA)PF_6 in DMF junction) as reference electrode (RE). Stationary and cyclic voltammetry (SV and CV) experiments performed on platinum rotating disk electrodes (RDE, EDI type, SOLEA-TACUSSEL) with potential scan rates in a 0.01−0.5 V s^{-1} range were run using a computerized DACFAMOV setting (MICROTEC-CNRS, Toulouse, France) connected to Apple II hardware. In this case, a classical three-electrode cell was employed with Pt disk (0.2 mm diameter) as WE, Pt wire as CE, and Ag/AgCl as RE. All potentials given hereafter will be referenced to this electrode and noted as V for V/Ag/AgCl. This electrode consisted of a Ag thread in an aqueous solution of saturated AgCl, separated from the cell by a fritted glass disk. This reference electrode has been tested for chloride leaks and the ferrocene/ferrocenium redox couple was measured at $E_{1/2} = 0.360$ V with $\Delta E_p = 59$ mV in dichloromethane ((TBA)PF_6 0.1 M) and at $E_{1/2} = 0.410$ V with $\Delta E_p = 60$ mV in DMF ((TBA)PF_6 0.1 M). Ferrocene was not added in solution during the measurements due to the presence of the copper(II/I) couple around 0.400 V. Spectrophotometric studies were performed on a diode array UV−visible spectrophotometer, Hewlett-Packard HP8452A, using 2 nm resolution. For spectroelectrochemical measurements, a homemade optical transparent thin-layer electrode (OTTLE) in Pyrex glass with an optical pathway of 0.1 mm was used. A platinum grid of 1000 mesh was employed as WE and a Ag/AgCl electrode was used as RE. The OTTLE placed in the HP 8452A spectrophotometer was monitored with a Bruker potentiostat and an IFELEC X-Y recorder.

Ligand 2. A mixture of catechol (44 mg, 0.4 mmol), 6-(bromomethyl)-2,2′-bipyridine (400 mg, 1.6 mmol), and potassium carbonate (332 mg, 2.4 mmol) in 40 mL of DMF was stirred under argon at 60 °C for 28 h. After removal of the solvent *in vacuo*, the residue was added to 75 mL of CH_2Cl_2, and the mixture was washed twice with 50 mL of H_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. Purification by column chromatography over silica gel (CH_2Cl_2, 2% MeOH) afforded **2** (131 mg, 0.29 mmol, 73%) as a white solid. ^1H NMR 300 MHz, acetone-d_6 δ, ppm: 8.67 (d, $J = 3.6$ Hz, 2H, $H_{6'}$), 8.48 (d, $J = 7.8$ Hz, 2H, $H_{3'}$), 8.40 (d, $J = 8.1$ Hz, 2H, H_3), 7.90 (m, 4H, $H_{4,4'}$), 7.70 (d, $J = 7.8$ Hz, 2H, H_5), 7.39 (m, 2H, $H_{5'}$), 7.17 (m, 2H, H_{cat}), 6.95 (m, 2H, H_{cat}), 5.37 (s, 4H, benzylic CH_2). ^1H NMR (300 MHz, $CDCl_3$) δ, ppm: 8.68 (ddd, $J = 1.0$ Hz, $J = 1.8$ Hz, $J = 4.8$ Hz, 2H, $H_{6'}$), 8.42 (dt, $J = 1.0$ Hz, $J = 7.9$ Hz, 2H, $H_{3'}$), 8.29 (dd, $J = 1.0$ Hz, $J = 7.9$ Hz, 2H, H_3), 7.80 (m, 4H, $H_{4,4'}$), 7.63 (dd, $J = 1.0$ Hz, $J = 7.9$ Hz, 2H, H_5), 7.30 (m, 2H, $H_{5'}$), 7.02 (m, 2H, H_{cat}), 6.91 (m, 2H, H_{cat}), 5.37 (s, 4H, benzylic CH_2). Anal. Calc for $C_{28}H_{22}N_4O_2 \cdot H_2O$ ($M_r = 464.5$): C, 72.49; H, 5.21; N, 12.06. Found: C, 72.34; H, 4.91; N, 11.71. Mp: 143−144 °C. Positive FAB mass spectrometry: calculated for $\{M\}^+ = [C_{28}H_{22}N_4O_2]^+$ *m/z* 446.5; measured for $I = 5.8$ V *m/z* 447.2 (100%).

[(2)Cu](CF_3SO_3)$_2$. Copper(II) triflate (10.8 mg, 0.03 mmol) was added to a solution of **2** (13.4 mg, 0.03 mmol) in 4 mL of CH_2Cl_2 and 7 mL of methanol. The resulting pale emerald green solution was stirred for 1 h. The copper(II) complex was precipitated by addition of 20 mL of hexane, collected by filtration, washed with hexane, and dried under reduced pressure to afford a pale green solid (20 mg, 0.025 mmol, 82%). Anal. Calc for $C_{30}H_{22}F_6N_4O_8S_2$ ($M_r = 808.2$): C, 44.59; H, 2.74; N, 6.93. Found: C, 44.72; H, 2.86; N, 6.98. UV−visible in CH_3CN, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 198 (75 000), 216 shoulder (39 100), 244 (27 500), 304 (29 600), 314 (29 400), 724 (98). Mp: 257 °C dec. Positive FAB mass spectrometry: Calculated for $\{M\}^+ = [C_{29}H_{22}F_3N_4O_5S]^+$: *m/z* 659.1; measured for $I = 7.4$ V *m/z* 658.1 (70%), 509.1 (100%) = [(**2**)CuH], 340.1 (21%) = [(**2**)Cu − CH_2bipy], 232.0 (77%) = [CH_2bipyCu]$^+$.

([(2)Cu]BF_4)$_n$ (*n* = 1, 2). Cu(CH_3CN)$_4$$BF_4$ (10.8 mg, 0.034 mmol) was added to a degassed solution of **2** (14.6 mg, 0.033 mmol) in 10 mL of dichloromethane. The resulting red solution was stirred under argon at room temperature for 1 h. The volume was reduced to 2 mL; then 10 mL of degassed Et_2O was added to precipitate the copper(I) complex. The product was collected by filtration, washed with Et_2O, and dried under reduced pressure to afford an air-stable orange solid (19 mg). ^1H NMR (300 MHz) of the two isomeric complexes (acetone-d_6), see Table 1. Anal. Calc for $C_{56}H_{44}N_8O_4Cu_2B_2F_8 \cdot CH_2Cl_2$ and $C_{28}H_{22}N_4O_2CuBF_4 \cdot {}^1/_2CH_2Cl_2$ (M_r = 1278.67 and 639.33): C, 53.54; H, 3.63; N, 8.76. Found: C, 53.50; H, 3.83; N, 8.76. UV−visible in CH_2Cl_2, λ_{max}, nm: 250, 266, 298, 448. (ϵ values were not calculated for the monomer/dimer mixture, as no deconvulation was carried out). Mp: 220 °C dec. Positive FAB mass spectrometry: Calculated for $\{M\}^+ = [C_{56}H_{44}N_8O_4Cu_2BF_4]^+$ *m/z* 1106.9 and $\{M'\}^+ = [C_{28}H_{22}N_4O_2Cu]^+$ *m/z* 509.1; measured for $I = 8.6$ V *m/z* 1107.1 (2%), 509.0 (100%), 340.0 = M^+ − CH_2bipy (15%), 232 = [CH_2bipy]$^+$ (55%). Distinction between $\{M\}^{2+}/2$ and $\{M'\}^+$ was possible due to their different isotopic patterns.

[(1)Cu_3](BF_4)$_3$. Cu(CH_3CN)$_4$$BF_4$ (12.1 mg, 0.038 mmol) was added to a degassed solution of CTV(bipy)$_6$ (**1**) (16.2 mg, 0.012 mmol) in 10 mL of dichloromethane. The resulting red solution was stirred under argon at room temperature for 1 h. The volume was reduced to 2 mL, and 10 mL of Et_2O was added to precipitate the copper(I) complex. The product was collected by filtration, washed with Et_2O, and dried under reduced pressure to afford an orange-red air-stable solid (19 mg, 0.01 mmol, 89%). ^1H NMR (300 MHz, acetone-d_6) δ, ppm: 6.97 (s, 3H, Ar H of CTV), 6.48 (s, 3H, Ar H of CTV), 5.44 (d, $J = 5.9$ Hz, 3H, CH_2bipy), 5.20 (d, $J = 5.9$ Hz, 3H, CH_2bipy), 5.08 (d, $J = 6.5$ Hz, 3H, CH_2bipy), 4.73 (d, $J = 6.5$ Hz, 3H, CH_2bipy), 4.40 (d, $J = 13.6$ Hz, 3H, CH_2 of CTV), 3.10 (d, $J = 13.6$ Hz, 3H, CH_2 of CTV). The aromatic bipyridine region was too complicated for interpretation; however, the ratio of aromatic bipyridine protons to methylene protons was correct. Anal. Calc for $C_{87}H_{66}N_{12}O_6Cu_3B_3F_{12} \cdot {}^3/_2\ CH_2Cl_2$ ($M_r = 1826.61$): C, 54.40; H, 3.56; N, 8.60. Found: C, 54.40; H, 3.70; N, 8.81. UV−visible in CH_2Cl_2, λ_{max} nm (ϵ, M^{-1} cm^{-1}): 438 (11 500). Mp: 239 °C dec. Positive FAB mass spectrometry: Calculated for $\{M\}^+ = C_{87}H_{66}N_{12}O_6Cu_3$ *m/z* 1739.0; measured for $I = 9.6$ V *m/z* 1738.8 (17%), 826.0 = [(**1**)Cu_3BF_4]$^{2+}/2$ (15%), 571.6 = [$\{M\}^+$ − 3CH_2bipe − BF_4]$^{2+}/2$ (100%).

[(1)Cu_3](CF_3SO_3)$_6$. Copper(II) triflate (15.7 mg, 0.043 mmol) was added to a solution of CTV(bipy)$_6$ (**1**) (19.7 mg, 0.014 mmol) in 7 mL of dichloromethane and 6 mL of methanol. The resulting yellow-green solution was stirred at room temperature for 2 h. The volume was reduced to 2 mL, and 12 mL of Et_2O was added to precipitate the copper(II) complex. The product was collected by filtration, washed with Et_2O, and dried under reduced pressure to afford a pale khaki green solid (20 mg, 0.008 mmol, 58%). Anal. Calc for $C_{93}H_{66}F_{18}N_{12}O_{24}S_6 \cdot 6H_2O$ ($M_r = 2568.65$): C, 43.49; H, 3.06; N, 6.54. Found: C, 43.38; H, 3.22; N, 6.48. UV-visible in CH_3CN, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 200 (173 100), 246 shoulder (73 400), 304 (73 600), 314 (70 600), 722 (173). Mp: 235 °C dec. Positive FAB mass spectrometry: Calculated for $\{M\}^+ = [C_{92}H_{66}N_{12}O_{21}S_5F_{15}]^+$ *m/z* 2311.5; measured for $I = 9.9$ V *m/z* 2311.8 (48%), 2162.4 = [$\{MH\}$ − $CF_3SO_3^-$]$^+$ (100%), 2013.0 = [$\{MH_2\}$ − 2$CF_3SO_3^-$]$^+$ (88%), 1863.2 = [$\{MH_3\}$ − 3$CF_3SO_3^-$]$^+$ (54%), 1694.6 = [$\{MH_3\}$− 3$CF_3SO_3^-$ − CH_2bipy]$^+$ (44%), 1482.1 = [$\{MH_3\}$ − Cu − 4$CF_3SO_3^-$ − CH_2bipy]$^+$ (57%), 1313.1 = ([$\{MH_3\}$ − Cu − 4$CF_3SO_3^-$ − (CH_2bipy)$_2$]$^+$ (58%), 1081.7 = [$\{M\}$ − $CF_3SO_3^-$]$^{2+}/2$ (35%), 1006.9 = [$\{MH\}$ − 2$CF_3SO_3^-$]$^{2+}/2$ (51%), 932.1 = [$\{MH_3\}$ − Cu − 5$CF_3SO_3^-$ − (CH_2bipy)$_3$]$^+$ (68%).

Results

Stoichiometric Studies. For both ligands, complexation stoichiometries were determined by *in situ* studies prior to the synthesis of the copper complexes on a preparative scale. Studies at concentrations higher than 10^{-3} M have not been performed due to the low solubility of the complexes formed.

(a) Copper(I) Complexes of 2. In CH_2Cl_2 and DMF, two absorption bands are observed in UV−visible spectroscopy at 236 nm (ϵ = 24 000 M^{-1} cm^{-1}) and 286 nm (ϵ = 33 000 M^{-1} cm^{-1}) for the free ligand **2**. The stoichiometry of the copper(I) complex formed was determined by electrochemical measurements. Monitoring the current intensity of the oxidation peak at +0.450 V (DMF) or +0.430 V (CH_2Cl_2) during the addition of increasing amounts of Cu(CH_3CN)$_4$$BF_4$ to a solution of **2** indicated a 1/1 or 2/2 stoichiometry. When samples of this complex obtained on preparative scale were dissolved in CH_2Cl_2 or in DMF, two oxidation peaks were observed in each of these solvents. The corresponding potentials were at 0.440 and 0.650 V in DMF and at 0.380 and 0.700 V in CH_2Cl_2. From

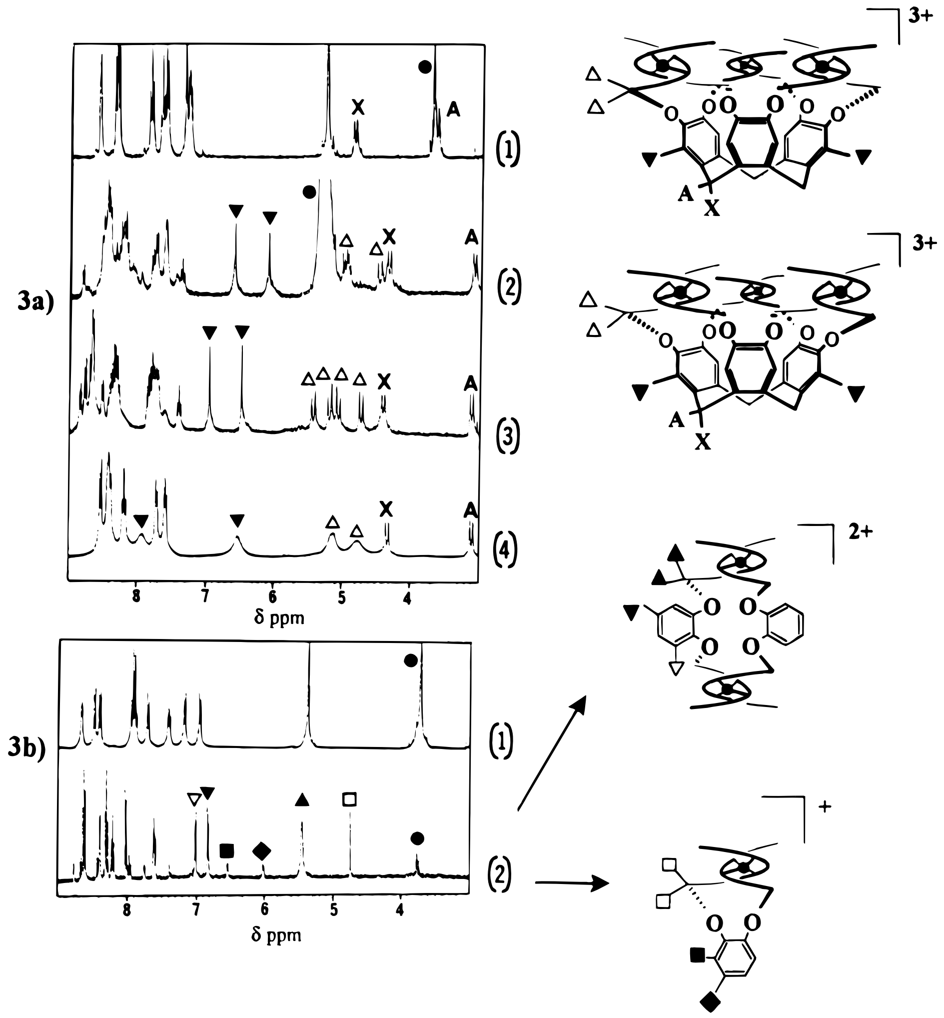

Figure 3. (a) Stacked plot of ^{1}H NMR spectra of ligand **1** (1) in $(CD_3)_2CO$ and its copper(I) complex in CD_2Cl_2 (2), $(CD_3)_2CO$ (3), and CD_3CN (4), at 300 MHz and room temperature. ● = solvent peak. (b) ^{1}H NMR spectra of free ligand **2** (1) and its copper(I) complexes (2) in $(CD_3)_2CO$, at 300 MHz and room temperature. ● = solvent peak.

mass spectrometry and ^{1}H NMR measurements (*vide infra*), it is clear that both the 1/1 and 2/2 (metal/ligand) complexes exist. Both species are detected in the mass spectrum, and the ion observed at *m*/*z* 509.0 which possesses an isotopic pattern corresponding to one copper atom was clearly assigned to the parent peak of the monomer and not to the doubly charged dimer. Thus the mono- and binuclear species, which correspond to at least two different coordination modes, are formed simultaneously. Even though the concentrations of both species could be obtained from NMR data, no deconvolution was carried out for the UV−visible spectrum of the complexes and respective molar extinction coefficients have not been calculated for the two complexes.

(b) Copper Complexes of 1. In UV−vis spectra, **1** exhibits two absorption bands at 238 nm ($\epsilon = 76\,000$ M^{-1} cm^{-1}) and at 288 nm ($\epsilon = 82\,000$ M^{-1} cm^{-1}) in CH_2Cl_2. The stoichiometry of the copper(I) complexation was determined by both UV−visible and electrochemical measurements. In both cases, increasing amounts of $Cu(CH_3CN)_4BF_4$ were added to solutions of **1** in CH_2Cl_2. UV−vis stoichiometric studies of copper(I) complexation were not carried out in DMF because of the copper(I) destabilization in this solvent. The 3/1 stoichiometric ratio of copper(I) to ligand **1** was determined by monitoring the absorbance variation at 438 nm as a function of the amount of copper added in CH_2Cl_2. The same stoichiometry could be determined by monitoring the current intensity for the oxidation peaks at +0.930 V in CH_2Cl_2 and at +0.800 V in DMF (Table 2). In both cases, complexation was completed when a ratio of 3 was reached for [Cu(I)]/[**1**]. Obviously, as two oxidation peaks are observed in CH_2Cl_2, electrochemistry indicates the presence of two types of complexes in solution. It should be pointed out that, upon addition of an excess of copper(I), only the oxidation peak corresponding to free copper(I) in solution was observed in addition to the oxidation of the complexes. Mass spectrometry measurements performed on the isolated copper(II/I) complexes exhibit only one molecular ion, indicating that the two species present in solution differ only in the coordination mode adopted by ligand **1**. Stoichiometric studies at higher concentration could not be performed because of the insolubility of the copper complexes in CH_2Cl_2 at concentrations higher than 10^{-3} M.

^{1}H NMR. (a) Copper(I) Complexes of 2. ^{1}H NMR of the copper(I) complexes in acetone-d_6 clearly shows a mixture of two isomers (Figure 3b(2)) which have been identified as the monomer and dimer compounds by mass spectrometry data. Evidence for a more abundant dinuclear versus mononuclear complex was obtained from CV studies discussed hereafter. Thus integration of the mixture's NMR spectrum in acetone indicates a 2/1 dimer/monomer ratio. This ratio appeared to be strongly dependent of the nature of the solvent. When ^{1}H NMR experiments were performed in DMF-d_7, a ratio of 7/1 (dimer/monomer) was observed. As a result of unfavorable tetrahedral geometry in the monomer, the aromatic catechol protons are shifted upfield (in both solvents) compared to the

Table 1. ^{1}H NMR Data for the Dimer/Monomer Mixture of the Complex ([**2**)Cu]$BF_4)_n$ in Acetone-d_6

	Proton							
	H3; H3′	H6′	H4	H4′	H5	H5′	CH_2(bipy)	H_{AB}(cat)
[(**2**)Cu]$_2^{2+}$: δ, multiplicity, *J* (Hz), integrn (au)	8.63, d, 8 Hz, 4H; 8.61, d, 8 Hz, 4H	8.39, d, 5 Hz, 4H	8.29, t, 3 Hz, 4H	8.21, td, 8 and 1.5 Hz, 4H	8.02, d, 8 Hz, 4H	7.62, m, 4H	5.45, br s, 8H	7.01 and 6.82, m, 4H each
[(**2**)Cu]$^+$: δ, multiplicity, *J* (Hz), integrn (au)	8.68, d, 8 Hz, 1H; 8.44, d, 8 Hz, 1H	8.79, d, 5 Hz, 1H	8.30, t, 8 Hz, 1H	7.97, t, 8 Hz, 1H	7.60, m, 1H	7.75, m, 1H	4.73, s, 2H	6.52 and 6.09, m, 1H each

same protons in the dimeric complex. Chemical shifts and coupling constants are listed in Table 1. No conclusion could be made concerning the structure of the dinuclear complex which can adopt a helicate type conformation or a "face-to-face" conformation. However, addition of chiral shift reagents like [Eu(fod)$_3$]$^{3+}$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioato) or Pirkle's reagent to the sample induced no change in the ^{1}H NMR spectrum, thus favoring the existence of a "face-to-face" isomer.

(b) Copper(I) Complexes of 1. The behavior of the complex [(**1**)Cu_3]$^{3+}$, in both ^{1}H NMR and electrochemical studies appeared to be strongly related to the coordinating ability of the solvent. The ^{1}H NMR spectra depicted in Figure 3a show the broadening of the signals corresponding either to the bipyridine subunits of ligand **1** or to the cyclotriveratrylene matrix in more coordinating solvents. The most significant ^{1}H NMR signal has been used for determining the number of species present in solution is the AX pattern of the methylene bridges in the CTV framework. In the spectrum of the pure free ligand **1** (Figure 3a(1)), this signal appears as two well-resolved doublets at 4.71 and 3.49 ppm. The aromatic protons of the CTV moiety appear as one singlet at 7.35 ppm, which is representative of the C_{3v} symmetry of the free ligand. The spectra of the copper(I) complex in different solvents, shown in Figure 3a, plots 2−4, exhibit only one set of AX signals, all located between 4.20 and 3.10 ppm. As previously reported in the literature for bipyridine−copper(I) helicates,[20] the CH_2 groups of the bipyridine are split into two AB signals (Δ) which are partially perturbed by the solvent peak in dichloromethane but clearly resolved in acetone. Thus, only one species could be detected in ^{1}H NMR. Also, the species produced still exhibits the C_3 symmetry axis of the CTV matrix, thus discarding the formation of the four possible meso forms of the copper(I) complex. Intramolecular motion of the bipyridines around the copper(I) ions is responsible for the splitting and/or broadening of the other signals, thus explaining the strong influence of the solvent. Additionally, for spectra recorded in dichloromethane-d_2 (Figure 3a(2)) and acetone-d_6 (Figure 3a(3)), which are poor coordinating solvents, the singlets observed respectively at 6.62, 6.13 and 6.97, 6.48 ppm are the result of the nonequivalence of the aromatic protons on the CTV framework induced by copper(I) coordination. Thus, only species of C_3 symmetry are observable and no other species of C_3 symmetry are present in an amount detectable by ^{1}H NMR technique. In acetonitrile-d_3, the two singlets of the aromatic protons of the CTV moiety are still detected at 6.62 and 7.89 ppm, and the broadening of these signals gave evidence for a solvent-aided enhanced motion of the bipyridine subunits around copper(I). The AX pattern remains well-defined, which is consistent with a concerted motion of the bipyridines, maintaining a permanent C_3 symmetry axis in the complexes.

Even though several isomers are possible for each complex, only one isomer, which definitely does not correspond to a meso form, is observable in ^{1}H NMR. As noticed during the titration of ligand **1** with a copper(I) salt monitored by electrochemistry, a minimum of two complexes is present in solution. As they exhibit different redox potentials, these two species cannot simply be enantiomers and they must therefore correspond to different coordination modes. From ^{1}H NMR, the relative concentration of the two species only allows for the detection of the major isomer and does not allow any conclusions to be drawn concerning the type of coordination mode preferred for [(**1**)Cu_3]$^{3+}$.

Electrochemical Studies. (a) Free Ligand 2. On a mercury electrode in DMF, the free ligand **2** shows two reduction steps at $E_{1/2} = -2.15$ and -2.68 V. The first step appears to be quasi-reversible ($E_{3/4} - E_{1/4} = 90$ mV) while the second reduction is irreversible. In oxidation, ligand **2** produces only one assisted oxidation of mercury at $E_{1/2} = +0.200$ V ($E_{3/4} - E_{1/4} = 30$ mV). On Pt and in CH_2Cl_2, no oxidation of **2** was detected up to +1.5 V.

(b) Free Ligand 1. On the mercury electrode in DMF, **1** shows two reduction steps at $E_{1/2}$ = -2.18 and -2.65 V. The first step meets the requirements for a quasi-reversible step ($E_{3/4} - E_{1/4} = 90$ mV), while the second reduction is irreversible. The oxidation of mercury facilitated by ligand **1** produces two assisted oxidation steps at respectively $E_{1/2} = 0.230$ V ($E_{3/4} - E_{1/4} = 30$ mV) and 0.350 V ($E_{3/4} - E_{1/4} = 50$ mV), the limiting current for the first wave being double that of the second. On Pt and in CH_2Cl_2 between -1.600 and 1.400 V, **1** was oxidized at $E_{pa} = +1.33$ V.

(c) Copper Complexes of 2. As expected from the characterization of the copper(I) complexes, two oxidation peaks assigned to the mono- and binuclear complexes have been detected for solutions of the synthetic complex ([(**2**)Cu]$BF_4)_n$ (Table 2). These oxidation peaks are observed at +0.440 and +0.650 V in DMF and at +0.380 and +0.700 V in CH_2Cl_2. In a first approach, neither NMR nor electrochemistry allows for identification of the redox couple corresponding respectively to the mononuclear or the binuclear species. However, the copper(II) complex formed with ligand **2** has been unambiguously characterized as the mononuclear species from mass spectrometry measurements. Furthermore, this mononuclear copper(II) species exhibits only one redox couple of which the reoxidation step (back scan regenerating Cu(II) from Cu(I)) is observed at $E_{pa} = +0.420$ V in DMF and at $E_{pa} = +0.370$ V in CH_2Cl_2 (Table 3). Thus, in the cyclic voltammogram of the mixture of ([(**2**)Cu]$_n(BF_4)_n$) complexes depicted in Figure 4, the oxidation peak in the mononuclear complex [(**2**)Cu]BF_4 could be identified as the peak at $E_{pa} = +0.440$ V in DMF and at $E_{pa} = +0.380$ V in CH_2Cl_2. From ^{1}H NMR measurements on the copper(I) complexes, it is clear that if there is an exchange between the mono- and binuclear forms, this exchange is slow on the NMR time scale.

However, in electrochemistry, the cyclic voltammograms are strongly affected by variations of the scan rate, thus indicating that the mono- and binuclear species are in exchange on the CV time scale. Formation of the complexes *in situ* afforded similar results. The main difference observed between redox studies on complexes generated *in situ* versus studies on the same isolated complexes is the slower exchange between the monomer and dimer in solutions of the isolated complexes. The exchange rate is enhanced by addition of increasing amounts of acetonitrile to solutions of [(**2**)Cu]BF_4. The single copper(II) complex existing with **2** is generated from the two copper(I) forms by coulometric oxidation to afford a very pale yellow

Table 2. Redox Potentials and Characteristics Measured for the Copper(I) Complexes of **1** and **2**[a]

complex		cyclic voltammetry at $v = 0.1$ V/s									
		DMF + (TBA)PF_6 (0.1 M)					CH_2Cl_2 + (TBA)PF_6 (0.1 M)				
		E_{pa}, V	E_{pc}, V	ΔE_p, mV	I_{pa}^B/I_{pa}^A	$(E_{pa} + E_{pc})/2$, V	E_{pa}, V	E_{pc}, mV	ΔE_p, mV	I_{pa}^B/I_{pa}^A	$(E_{pa} + E_{pc})/2$, V
$[(\mathbf{2})Cu]_n^{n+}$	$n = 1$ or "int"	+0.450	+0.370	80		+0.410	+0.430	+0.350	80		+0.390
in situ	$n = 2$ or "vic"						+0.660			0.5	
$[(\mathbf{2})Cu]_n^{n+}$	$n = 1$ or "int"	+0.440	+0.360	80		+0.400	+0.380	+0.320	60		+0.350
isolated	$n = 2$ or "vic"	+0.650					+0.700	+0.580	120	10	+0.640
$[(\mathbf{1})Cu_3]^{3+}$	"int"	+0.460	+0.360	100		+0.410	+0.460	+0.320	140		+0.390
in situ	"vic"	+0.800			3.7		+0.930	+0.680	250	9.9	
$[(\mathbf{1})Cu_3]^{3+}$	"int"		+0.350	290			+0.400	+0.330	70		+0.365
isolated	"vic"	+0.640					+0.860	+0.680	180	8.0	

[a] V refers to V vs Ag/AgCl.

Table 3. Redox Potentials and Characteristics Measured for the Copper(II) Complexes of **1** and **2**[a]

complex		cyclic voltammetry at $v = 0.1$ V/s									
		DMF + (TBA)PF_6 (0.1 M)					CH_2Cl_2 + (TBA)PF_6 (0.1 M)				
		E_{pa}, V	E_{pc}, V	ΔE_p, mV	I_{pa}^B/I_{pa}^A	$(E_{pa} + E_{pc})/2$, V	E_{pa}, V	E_{pc}, V	ΔE_p, mV	I_{pa}^B/I_{pa}^A	$(E_{pa} + E_{pc})/2$, V
$[(\mathbf{2})Cu]_n^{2n+}$	$n = 1$ or "int"	+0.450	+0.370	80		+0.410	+0.400	+0.310	90		+0.355
in situ	$n = 2$ or "vic"										
$[(\mathbf{2})Cu]_n^{2n+}$	$n = 1$ or "int"	+0.420	+0.330	90		+0.375	+0.370	0.280	90		+0.325
isolated	$n = 2$ or "vic"										
$[(\mathbf{1})Cu_3]^{6+}$	"int"	+0.460	+0.350	110		+0.405	+0.390	+0.230	160		+0.310
in situ	"vic"	+0.600			1.7		+0.870			1.8	
$[(\mathbf{1})Cu_3]^{6+}$	"int"	+0.450	+0.320	130		+0.385	+0.350	+0.220	130		+0.285
isolated	"vic"										

[a] V refers to V vs Ag/AgCl.

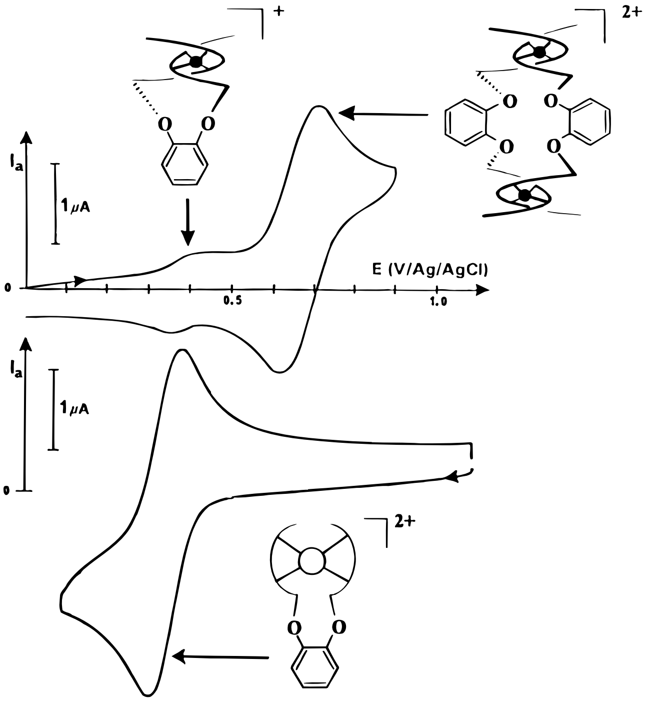

Figure 4. Electrochemical identification of the mono- and binuclear complexes of **2** with copper(I) (black circle) and copper(II) (white circle) in CH_2Cl_2, 0.1 M in (TBA)PF_6, at 0.1 V s^{-1}.

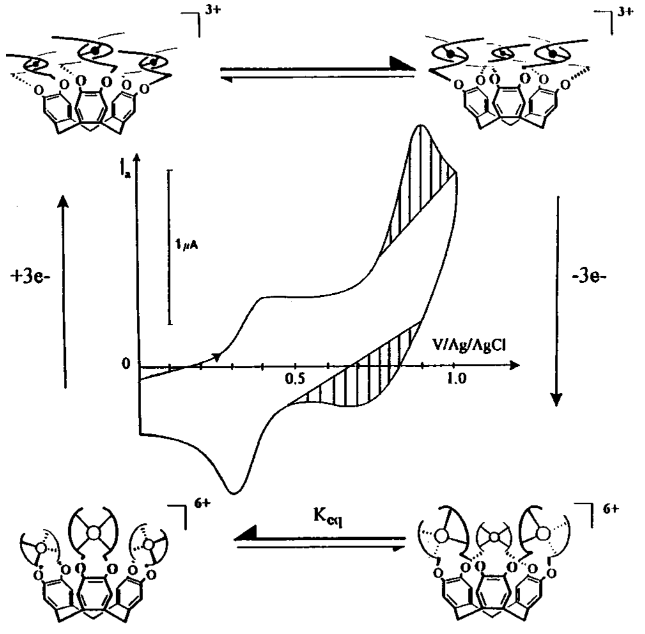

Figure 5. Typical cyclic voltammogram obtained for $[(\mathbf{1})(Cu)_3]^{3+}$ isolated on a preparative scale and schematic representation of the species involved in the electrochemically triggered conformational rearrangement in CH_2Cl_2, 0.1 M in (TBA)PF_6, 0.1 V s^{-1} and 293 K: Cu(I), black circle; Cu(II), white circle. The hatched peaks correspond to the "vic" coordination mode, and the unhatched peaks correspond to the "int" coordination mode.

solution which exhibits a single redox couple centered at $(E_{pa} + E_{pc})/2 = +0.375$ V in DMF and +0.325 V in CH_2Cl_2 (same redox potentials as those measured—Figure 4—for the isolated copper(II) complex of **2**).

(d) Copper Complexes of 1. (1) Synthetic Copper Complexes. A typical voltammogram obtained from CV of the isolated complexes $[(\mathbf{1})Cu_3](BF_4)_3$ in CH_2Cl_2 + (TBA)PF_6 (0.1 M) is represented in Figure 5 and is discussed hereafter. In CH_2Cl_2, two peaks are observed in both oxidation and reduction. Thus, for the initial copper(I) complex, two complex forms, one minor and one major, corresponding to two different coordination modes, are present in solution.

In DMF + (TBA)PF_6 (0.1 M), only the more stable complex is observed (Table 2). Variation of the scan rate in cyclic voltammetry did not lead to severe changes in the shape of the voltammograms; redox potentials for the oxidation and back-reduction peaks were unaffected in CH_2Cl_2 and slightly shifted in DMF. The above results indicate that, in CH_2Cl_2, the copper(I) species are in fast exchange on the cyclic voltammetry time scale. Exhaustive oxidation of this copper(I) complex at +1.0 V in DMF decreased the current intensity to the limiting value of zero, the number of electrons involved in the process being estimated to 3. After exhaustive oxidation, the reduction potential observed and the two oxidation steps are the same as for copper(II) complex of **1** (see Table 3). Exhaustive oxidations were also performed in CH_2Cl_2 with the complex $[(\mathbf{1})Cu_3]^{3+}$ at +1.1 V. Before exhaustive oxidation, two peaks were observed in both oxidation and reduction (Table 2), while after coulometric oxidation only one reduction peak at +0.230 V (associated with two oxidation peaks at +0.390 and +0.870 V) remained.

(2) *In Situ* Copper Complexes. Surprisingly, from copper(I) complexes formed in situ with **1** in CH_2Cl_2, it has not been possible to electrogenerate a stable corresponding copper(II) complex. Exhaustive coulometric oxidations were performed at +0.500 and +1.200 V in CH_2Cl_2 + $(TBA)PF_6$ (0.1 M). Despite a considerable decrease of the current intensity, the zero current was never reached during coulometric oxidation at +0.500 V; this is to be expected if an exchange of conformation occurs between the two complexed forms. The UV−visible spectrum of the "oxidized" solution was identical to the spectrum of the starting copper(I) complex. The spectrum of the oxidized complex $[(\mathbf{1})Cu_3]^{6+}$ was only observed after exhaustive oxidation at +1.200 V of the corresponding copper(I) complex on an optically transparent thin layer electrode during spectroelectrochemical measurements. The relative instability of these copper(II) complexes of **1** electrogenerated in situ has been attributed to the 4 equiv of acetonitrile still present in solution during the in situ complexation process. This hypothesis was verified by adding increasing amounts of CH_3CN to a solution of synthesized $[(\mathbf{1})Cu_3]^{3+}$. Beyond a certain concentration of acetonitrile, the reduction peak at E_{pc} = 0.680 V is no longer observed.

In contrast with the results obtained in CH_2Cl_2, for copper(I) complexes of **1** formed in situ in DMF + $(TBA)PF_6$ (0.1 M) it was possible to produce a stable corresponding copper(II) complex. When coulometric measurements were performed at +1.200 V, the limiting value of zero was reached and the number of electrons involved in the process could be estimated to 3. The UV−visible spectrum of the oxidized $[(\mathbf{1})Cu_3]^{3+}$ was identical to the spectrum of the complex $[(\mathbf{1})Cu_3]^{6+}$ generated in situ from $Cu(CF_3SO_3)_2$ and **1**. Exhaustive reduction at +0.100 V of this oxidized solution containing the copper(II) complex regenerated from the initial copper(I) complex $[(\mathbf{1})Cu_3]^{3+}$. The UV−visible spectrum of this regenerated species was identical to the spectrum of the starting copper(I) complex of **1**. The hypothesis of an equilibrium between distinct copper(I) complexes and also between distinct copper(II) complexes has been verified by variable-temperature cyclic voltammetry studies described hereafter.

Variable-Temperature Cyclic Voltammetry. Significant voltammograms concerning the evolution of the redox potentials, recorded for the mixture of two distinct copper(I) species of **1**, are depicted in Figure 6. As described above, at room temperature (dashed line in Figure 6), the oxidation of the minor copper(I) conformer is observed at +0.400 V in CH_2Cl_2 and is followed by the oxidation of the major copper(I) conformer at +0.860 V in this solvent. During the return scan, one minor copper(II) conformer is reduced at +0.680 V while a major copper(II) conformer is reduced at +0.330 V.

At 260 K (solid line in Figure 6), considerable changes already occur in the shape of the voltammograms. The first oxidation peak corresponding to the minor copper(I) conformer has nearly disappeared while the second oxidation peak corresponding to the major copper(I) conformer is noticeably broadened and shifted to +0.770 V. On the return scan at 260 K, the reduction peak corresponding to the minor copper(II) conformer is more intense and also shifted to a less anodic potential of +0.620 V. The reduction peak assigned to the major copper(II) conformer is broadened and shifted to +0.200 V. At 220 K (semidotted line in Figure 6) and lower temperatures, only one copper(I) conformer is observed and oxidized at +0.720 V. The corresponding copper(II) conformer is reduced at +0.530 V.

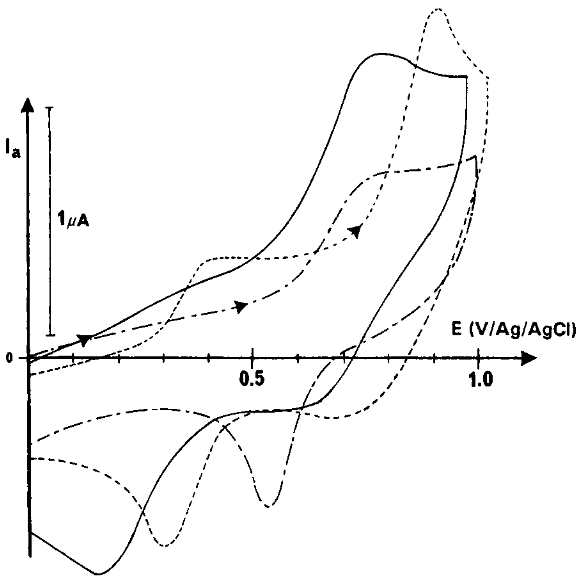

Figure 6. Variable-temperature cyclic voltammetry and species involved in CH_2Cl_2, 0.1 M in $(TBA)PF_6$, at 0.1 V s^{-1}: 293 K (- - -); 260 K (—); 220 K (- • -).

Discussion

For the isolated complex $[(\mathbf{1})Cu_3](BF_4)_3$, only one pair of enantiomers out of the eight possible isomers (see Figure 2) has been observed in ^1H NMR experiments. This is in agreement with a CPK model examination which shows that the δ or λ twist occurring in one $[(bipy)_2Cu^I]$ subunit is necessarily transmitted to the neighboring $[(bipy)_2Cu^I]$ for steric reasons. This is also clear from the ^1H NMR data, as no meso form resulting from mixed δ or λ twists is observed. Indeed, the presence of such meso complexes would result in more than two singlets for the aromatic protons of CTV and also more than one AX pattern. In noncoordinating solvents, like CD_2Cl_2 or $(CD_3)_2CO$, the conformational exchange, if there is one, is slow compared to the NMR time scale. In a coordinating solvent such as CD_3CN the motion of bipyridines around copper(I) ions is facilitated by the availability of coordinating solvent molecules which can enter the inner coordination sphere of the metal upon partial dissociation of the bipyridine moieties. The stacked plots in Figure 3a clearly show the progressive broadening of the two singlets corresponding to aromatic protons of the CTV framework, which is consistent with a greater mobility of the bipyridines in coordinating solvents. Attempts to observe the minor conformer by variable-temperature (VT) ^1H NMR experiments in dichloromethane-d_2 and acetonitrile-d_3 did not lead to assignable peak splittings in the spectra. However, between 269 and 247 K, in dichloromethane, small side peaks in the Ar H pattern of the CTV (δ 6.62 and 6.13) were observed, while the bipyridine region of the spectrum became much better resolved. No assignment has been possible so far, and because of the low solubility of the copper(I) complexes in noncoordinating solvents, 2D ^1H NMR experiments remained unsuccessful. In acetonitrile, VT experiments down to 247 K simply lowered the resolution of the bipy region and shifted the Ar H signals of the CTV, but no significant signal splittings occurred.

The stoichiometry expected for the formation of copper(I) trinuclear complexes of **1** has been confirmed by both UV−visible techniques and electrochemical methods. For ligand **1**, electrochemical studies of the complex formed have demonstrated the presence of two types of complexes, respectively oxidized at +0.400 and +0.860 V in CH_2Cl_2 (see Figure 5), whereas only one oxidation peak is observed at +0.640 V in DMF (Table 2). The two expected return peaks are observed at +0.680 and +0.330 V in CH_2Cl_2, while one return peak at +0.350 V is observed in DMF. The respective current intensities of the peaks are not in agreement with a reversible system. The typical voltammogram reproduced in Figure 5 shows that the algebraic sum of the current intensities of the set of oxidation peaks is close to the algebraic sum of the current intensities for the return peaks.

As opposed to the NMR spectra, two conformers could be distinguished in CH_2Cl_2 by electrochemistry, which can be considered as a more sensitive method. During the electrochemical determination of the conformer mixture, the characteristic oxidation detecting one conformer influences the equilibrium between the two species. Thus, the minor conformer, oxidized at the less anodic potential, appears more abundant, which is confirmed by the scan rate dependence of the conformer ratio determined by electrochemical methods. Consequently, correlations between the relative concentration of different conformers determined by ^{1}H NMR and electrochemistry would not be reliable.

However, as illustrated by the current intensities in Figure 5, the minor conformer is more easily oxidized than the major conformer. This is easily explained when one considers that the Cu(II)/Cu(I) redox potential is dependent on the more or less tetrahedral geometry of the cuprous ion (*i.e.*, oxidation will be more difficult for a more ideal tetrahedral coordination mode). In a first analysis, examination of molecular models, ^{1}H NMR and electrochemistry suggest that the minor isomer is most likely $[(\mathbf{1})^{int}Cu_3]^{3+}$, which provides the most distorted tetrahedral coordination sphere for copper(I). In the major conformer $[(\mathbf{1})^{vic}Cu_3]^{3+}$, the coordinating bipy groups are attached to two adjacent catechol subunits, consequently allowing the entwining of the methylbipyridyl groups to provide a regular tetrahedral coordination sphere for the cuprous ion.

The ratio between the two isomers, which are actually conformers, in solution, could be estimated to a minimum of 10/1 by comparison of the respective peak currents in the cyclic voltammograms, for each solvent. Upon oxidation, the change in the preferred coordination geometry, from tetrahedral Cu(I) to square planar Cu(II) inverts the conformer ratio. For the Cu(II) complex, the bipy groups provide the less distorted square planar geometry when located on the same catechol subunit, and reciprocally, the least stable conformer $[(\mathbf{1})^{vic}Cu_3]^{6+}$ is obtained when the bipy groups are located on two adjacent catechol subunits. The rapid exchange between the two conformers of the Cu(II) complex explains the inversion in the intensity ratio for the return peaks observed in cyclic voltammetry. Coulometric measurements have confirmed this hypothesis, by determining the number of electrons exchanged upon running an electrolysis at +0.500 V (oxidizing the least stable conformer) and running the same experiment at +1.200 V (oxidizing both conformers).

The electrochemical studies of the copper(I) and copper(II) complexes of **2** have permitted the unambiguous assignment of the two oxidation peaks observed in the cyclic voltammogram of $[(\mathbf{1})Cu_3](BF_4)_3$. The formation in situ of $[(\mathbf{2})Cu]BF_4$ by addition of 1 equiv of copper(I) tetrakis(acetonitrile) tetrafluoroborate to a solution of **2** in CH_2Cl_2 leads to the observation of two oxidation peaks at +0.430 and +0.660 V in the corresponding cyclic voltammogram, with only one return peak at +0.350 V. Again, this corresponds to the formation of two different types of complexes represented in Figure 2c. In the distorted monomeric complex, copper(I) is easily oxidized to copper(II) due to the disfavored tetrahedral arrangement of the bipyridines around the metal ion. In the dimeric complex, the coordinating bipyridines are on separate catechols, thus diminishing the distortion of the tetrahedral copper(I) geometry. Consequently, copper(I) in the binuclear complex is more difficult to oxidize. This time, the two types of complexes are not in fast exchange, either on the ^{1}H NMR or on the cyclic voltammetry time scales, thus allowing for the characterization of each complex, not only by CV and ^{1}H NMR but also by positive FAB mass spectrometry. Amazingly, the oxidation of both complexes generates a unique type of copper(II) complex. This has been experimentally verified in two different ways. First, the exhaustive coulometric oxidation of a solution of $[(\mathbf{2})Cu]_n^{n+}$ in DMF yielded a stable solution of $[(\mathbf{2})Cu]^{2+}$, which exhibited only one reversible couple at +0.380 V, corresponding to the reversible couple observed in the cyclic voltammagroms of $[(\mathbf{2})Cu]^{2+}$. Exhaustive coulometric reduction at +0.100 V of the $[(\mathbf{2})Cu]^{2+}$ in situ complex in DMF + $(TBA)PF_6$ (0.1 M) afforded a red-orange solution of a copper(I) complex. This time, the copper(I) solution exhibited only one reversible redox couple corresponding to the monomeric copper(I) complex centered at +0.410 V, as DMF favors the formation of the copper(II) complex which exists as a monomer in solution. Secondly, the copper(II) complex prepared with ligand **2**, which has been characterized as a monomer, exhibits a single redox couple centered at +0.375 V. This copper(II) complex can be converted to the corresponding copper(I) complex by coulometric reduction. The resulting solution exhibits the same voltammogram as the solution of copper(I) complexes prepared separately.

Consequently, we can establish that, in the case of $[(\mathbf{1})Cu_3](BF_4)_3$, the minor isomer observed in electrochemistry is $[(\mathbf{1})^{int}Cu_3]^{3+}$. Figure 5 summarizes the conformational transformations occurring in the system during one voltammetric cycle. In the copper(I) state, the two conformers are in equilibrium. Apparently, the rate of exchange between the two conformers is strongly dependent on the coordinating power of the solvent. Upon a scan toward anodic potentials in CH_2Cl_2, the first peak observed at +0.400 V is the oxidation of the less stable conformer, which possesses the most distorted tetrahedral geometry for the copper(I) ions. The second peak at +0.860 V corresponds to the oxidation of the most stable conformer which provides the less distorted tetrahedral geometry for the cuprous ions. After conversion of all the material into the copper(II) forms, scanning toward less anodic potential reveals that the vicinal conformer has almost disappeared. With the complexes formed in situ but not with the complexes isolated on a preparative scale, only a small reduction peak is observed at +0.680 V even at high scan rates. The decoordination−recoordination process converting the destabilized conformer into the stable conformer is extremely fast and accelerates as the affinity of the solvent for copper increases. The second return peak at +0.330 V corresponds to the reduction of the internal copper(II) complex in which the bipyridines are located on the same catechol subunit. In fact, the potential observed for this reduction is very close to the reduction potential of the complex $[(\mathbf{2})\mathrm{Cu}]^{2+}$, which is consistent with the coordination mode assigned for each conformer of $[(\mathbf{1})\mathrm{Cu}_3]^{3+}$.

In summary, the copper(II/I) complexes of **1** represent a bistable system in which the interconversion between the stable forms $[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{3+}$ and $[(1)^{\mathrm{int}}\mathrm{Cu}_3]^{6+}$ is electrochemically triggered and corresponds to the decoordination−rotation−recoordination of at least three bipyridines. The driving force for this conformational isomerization is the search for the most stable arrangement of the bipyridines around the copper ion in two redox states. The bistability of this system is best observed by cyclic voltammetry in coordinating solvents such as DMF or CH_3CN, which facilitates the "int"−"vic" rearrangement, or at low scan rates in CH_2Cl_2. Thus, the equilibrated system of copper complexes $[(\mathbf{1})\mathrm{Cu}_3]^{6+/3+}$ presents a potential-dependent conformational hysteresis.[27,28] In this sense, it compares with systems presenting constitutional hysteresis,[28] translational isomerism in [2]-catenanes,[29] or electrochemically triggered swinging of [2]-catenates.[30]

Thermodynamic information concerning the equilibrium between the two coordination isomers $[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{6+}$ and $[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{6+}$ was obtained from the changes observed for the reduction peak currents I_{pc} in cyclic voltammograms recorded at variable temperature. In the global scheme of Figure 5, the redox system int corresponds to the signals around +0.4 V, and the system vic corresponds to those around +0.8 V. The ratio $I_{\mathrm{pc}}(\mathrm{vic})/I_{\mathrm{pc}}(\mathrm{int})$ measured at scan rates (v) low enough to make the ratio independent of v provides direct access to the equilibrium constant $K_{\mathrm{eq}} = [[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{6+}]/[[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{6+}]$ at any temperature. This method applied to the currents $I_{\mathrm{pc}}(\mathrm{int})$ and $I_{\mathrm{pc}}(\mathrm{vic})$ measured on cyclic voltammograms recorded at temperatures ranging from 241 to 293 K yielded equilibrium constant values $K_{\mathrm{eq}} = [[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{6+}]/[[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{6+}]$ ranging from 7.3 at 295 K to 0.4 at 241 K. Thus, van't Hoff analysis of the ln K_{eq} versus $1/T$ plot from a set of K_{eq} values calculated at various temperatures provides the values of $\Delta H = +34 \pm 1$ kJ mol^{-1} and $\Delta S = +136.0 \pm 0.5$ J mol^{-1} K^{-1} as characteristic of this equilibrium.[31] A similar quantitative analysis was not possible for the equilibrium between the two coordination isomers of copper(I), $[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{3+}$ and $[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{3+}$, because the oxidation peak current $I_{\mathrm{pa}}(\mathrm{int})$ of $[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{3+}$ (Figure 6) became too small as soon as T dropped below 273 K. The equilibrated reaction from $[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{6+}$ to $[(\mathbf{1})^{\mathrm{int}}\mathrm{Cu}_3]^{6+}$ is an endothermic reaction. As this reaction leads to a less distorted (int) square planar coordinated Cu(II) than in the initial tetrahedral (vic) Cu(II) complex, the observed ΔS cannot be accounted for by this change in coordination mode. A higher degree of flexibility of each $\mathrm{Cat(bipy)}_2\mathrm{Cu}^{\mathrm{II}}$ subunit in the "int" coordination mode may possibly explain the increase in entropy. In the equilibrium process, the negative free energy ($\Delta G = -6.53$ kJ mol^{-1}) is representative of a spontaneous displacement toward the more stable, and less distorted "int" coordination mode for the copper(II) complex. It is clear that this observed negative free energy change is driven by the positive reaction entropy. The same phenomenon is expected to influence the equilibrium between the copper(I) coordination modes, and in fact, it does favor the $[(\mathbf{1})^{\mathrm{vic}}\mathrm{Cu}_3]^{3+}$ form in both CH_2Cl_2 and DMF. The kinetics involved in the conversion of "vic" into "int" species for copper(II) complexes and "int" into "vic" species in the case of copper(I) complexes are too fast to be measured by conventional methods. Further studies are necessary, particularly to determine the exact contributions of the solvent and eventual anionic species in the decoordination−recoordination process converting "vic" forms into "int" species and vice versa.

Conclusion

The combination of electrochemical methods with standard ^{1}H NMR and mass spectrometry has allowed full characterization of the components of a new bistable system of copper complexes obtained with ligands based on bipyridines and cyclotriveratrylene. Both ligands, **1** and **2**, afforded a set of complexes that exhibit an electrochemical potential hysteresis through conformational isomerism. The species involved in the unexpected bistable system produced with ligand **2** have been useful reference models for the characterization of the species produced with ligand **1**, but the full understanding of this unexpected system is complicated by the changing molecularity involved in the process producing the more stable $[(\mathbf{2})\mathrm{Cu}]_2^{2+}$ from two $[(\mathbf{2})\mathrm{Cu}]^{+}$. The system generated with ligand **1** is only based on conformational isomerism, which makes it simpler to study, and preliminary thermodynamic data have been obtained. Fast kinetics measurements and introduction of additional substituents on the bipyridine units in order to slow the rates of conversion in complexes of ligand **1** are in progress.

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Supporting Information Available: Figures showing the variation of the absorbance band at 438 nm upon addition of copper(I) to **1** in dichloromethane and Van't Hoff analysis of the data obtained from variable-temperature cyclic voltammetry (2 pages). Ordering information is given on any current masthead.

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