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Copper Complexes Generated from Ferrocene−Bipyridyl Metallo-Synthons

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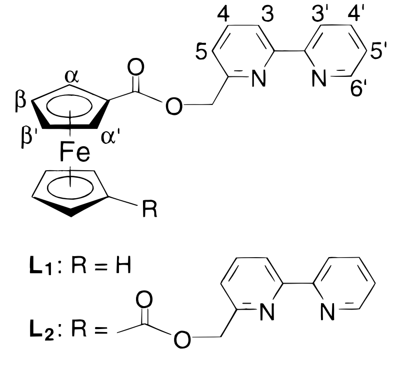
Introduction

Design and synthesis of host molecules containing metallocene units which could accommodate a particular metal ion at its coordination site and undergo a concurrent redox change have attracted considerable attention in host−guest chemistry.[1] Another feature of these inorganic receptors is the possibility to construct molecular structures that contain two or more different coordinated metal ions, which are of interest in many biological and catalytic processes.[2] Most of these studies focus on macrocyclic derivatives of metallocenes with relatively few systems based on ferrocenes functionalized with 2,2′-bipyridyl (bipy) arms,[2,3] which allow us to extend complexation studies to transition metal cations. We report here complexation studies of Cu^{I} and Cu^{II} cations with novel 1-bipyridyl and 1,1′-bis(bipyridyl) ester-bridged derivatives of ferrocene, $\mathbf{L_1}$ and $\mathbf{L_2}$ (Chart 1), and demonstrate that $\mathbf{L_2}$ forms a mixed tetranuclear helicate with copper(I) cations in the solid state.

Experimental Section

Ligands. $\mathbf{L_1}$ and $\mathbf{L_2}$ were prepared by the stoichiometric reaction of 6-(hydroxymethyl)-2,2′-bipyridine[4] with 1 mmol of chlorocarbonylferrocene[5] and 1,1′-bis(chlorocarbonyl)ferrocene,[6] respectively, in 10 mL of dried toluene containing 2 and 4 mmol of freshly distilled triethylamine, respectively. The reaction mixture was stirred overnight at room temperature under an inert atmosphere, then filtered and evaporated to dryness. The crude product was extracted with CH_2Cl_2, and the organic phase was washed with H_2O. The solvent was removed in vacuo, affording a crude orange-brown solid which was purified by neutral alumina column chromatography eluted with CH_2Cl_2, to yield $\mathbf{L_1}$ (85%) and $\mathbf{L_2}$ (78%) as orange solids.

Chart 1



$\mathbf{L_1}$. ^{1}H NMR (CD_2Cl_2) δ, ppm/TMS: 4.18 (*H*-Cp, s, 5H), 4.43 ($H_{\beta,\beta'}$, t, 2H), 4.87 ($H_{\alpha,\alpha'}$, t, 2H), 5.41 (-O-*CH*$_2$-bipy, s, 2H), 7.31 (*H4′*, m, 1H), 7.48 (*H5′*, d, 1H), 7.85 (*H4,5*, m, 2H), 8.38 (*H3′*, d, 1H), 8.48 (*H3*, d, 1H), 8.65 (*H6′*, d, 1H). UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 443 (241). FAB-MS, *m*/*z*: 399 $(M + H)^+$. Anal. Calcd (found) for $C_{22}H_{18}N_2O_2Fe$ (M_r = 398.248): C, 66.35 (66.05), H, 4.56 (4.39), N, 7.03 (6.86).

$\mathbf{L_2}$. ^{1}H NMR (CD_2Cl_2) δ, ppm/TMS: 4.44 ($H_{\beta,\beta'}$, t, 4H), 4.90 ($H_{\alpha,\alpha'}$, t, 4H), 5.39 (-O-*CH*$_2$-bipy, s, 4H), 7.30 (*H4′*, m, 2H), 7.48 (*H5′*, d, 2H), 7.77 (*H4,5*, m, 4H), 8.34 (*H3′*, d, 2H), 8.43 (*H3*, d, 2H), 8.63 (*H6′*, d, 2H). UV−vis (CH_3CN) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 450 (337). FAB-MS, *m*/*z*: 611 $(M + H)^+$. Anal. Calcd (found) for $C_{34}H_{26}N_4O_4Fe$ (M_r = 610.457): C, 66.90 (66.79), H, 4.29 (4.03), N, 9.18 (8.95).

Complexes. Copper complexes were synthesized as their perchlorate salts by the reaction at room temperature in CH_2Cl_2 of stoichiometric amounts of $\mathbf{L_1}$ ($\mathbf{L_1}$ + 0.5 Cu) and $\mathbf{L_2}$ ($\mathbf{L_2}$ + 1 Cu) and $[Cu(CH_3CN)_4]ClO_4$ or $Cu(ClO_4)_2{\cdot}6H_2O$ respectively, precipitated upon addition of diethyl oxide, and collected as orange solids by succion filtration. **Warning!** *Perchlorate salts are hazardous because of the possibility of explosion*. MS (FAB and electrospray) spectra of isolated Cu^{I} or Cu^{II} complexes display exclusively the *m*/*z* peaks at 859 (2$\mathbf{L_1}$ + Cu) and 673 ($\mathbf{L_2}$ + Cu) corresponding to the monomeric cationic complexes without counteranions, with the expected isotopic profile without contanimation from dinuclear or polymeric structures. X-ray-quality crystals of the complex formed between $\mathbf{L_2}$ and $[Cu(CH_3CN)_4]BF_4$ were obtained by vapor diffusion of diethyl ether into an acetonitrile/dichloromethane solution of the copper(I) complex.

$\mathbf{[Cu(L_1)_2](ClO_4)}$. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 441 (1062). Anal. Calcd (found) for $C_{44}H_{36}N_4O_4Fe_2CuClO_4$ (M_r = 959.492): C, 55.08 (54.79), H, 3.78 (3.52), N, 5.84 (5.77).

$\mathbf{[Cu(L_1)_2](ClO_4)_2}$. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 451 (356), 690 (ca. 60); EPR (frozen DMSO): $g_{\parallel} = 2.28$, $g_{\perp} = 2.09$, $A_{\parallel} = 125 \times 10^{-4}$ cm^{-1}. Anal. Calcd (found) for $C_{44}H_{36}N_4O_4Fe_2CuCl_2O_8{\cdot}CH_3CN$ (M_r = 1058.943 + 41.053): C, 50.23 (50.12), H, 3.57 (3.31), N, 6.37 (6.16).

$\mathbf{[Cu_2(L_2)_2](ClO_4)_2}$. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 445 (5040). Anal. Calcd (found) for $C_{68}H_{52}N_8O_8Fe_2Cu_2Cl_2O_8$ (M_r = 1546.908): C, 52.80 (52.62), H, 3.39 (3.19), N, 7.24 (7.06).

$\mathbf{[Cu(L_2)](ClO_4)_2}$. λ_{max}, nm (ϵ, M^{-1} cm^{-1}) 452 (830), 700 (208); EPR (frozen DMSO) $g_{\parallel} = 2.27$, $g_{\perp} = 2.07$, $A_{\parallel} = 150 \times 10^{-4}$ cm^{-1}. Anal. Calcd (found) for $C_{34}H_{26}N_4O_4FeCuCl_2O_8{\cdot}CH_3CN$: C, 47.31 (47.02), H, 3.20 (2.92), N, 7.66 (7.43).

Reagents, Instrumentation, and Procedure. Acetonitrile (Rathburn, HPLC grade) was used as received. Dichloromethane was dried over neutral alumina (activity I) for at least 6 days. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka, recrystallized from ethyl acetate−cyclohexane, and dried under vacuum at 80 °C for 3 days. Electrochemical experiments were conducted in a conventional three-electrode cell under an argon atmosphere at 20 °C. The Ag/10 mM $AgNO_3$ + 0.1 M TBAP in CH_3CN was used as a reference electrode. The $AgNO_3$ solution was separated from the working compartment by a salt bridge. The potential of the regular Fc/Fc^+ redox couple used as an internal standard was 0.07 V under

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Table 1. Cyclic Voltammetric Data[a] for Ligands and Their Copper Complexes

	L_1			L_2		
	free L_1	$2L_1$ + Cu		free L_2	L_2 + Cu	
solvent	Fc/Fc$^+$	Fc/Fc$^+$	Cu^I/Cu^{II}	Fc/Fc$^+$	Fc/Fc$^+$	Cu^I/Cu^{II}
CH_3CN	0.33 (70)	0.38 (60)	0.19 (60)	0.56 (60)	0.71 (70)	0.10 (80)
CH_2Cl_2	0.45 (110)	[b]	0.33 (60)	0.69 (110)	0.84 (90)	0.23 (150)

[a] $E_{1/2}$, V vs Ag/AgNO$_3$, 0.01 M + CH_3CN + TBAP 0.1 M (ΔE_p, mV); $\upsilon = 0.1$ V s^{-1}; IR drop has been estimated to 12 mV in CH_3CN electrolyte from impedance spectroscopy measurements. [b] Strong adsorption phenomena precluded determination of $E_{1/2}$.

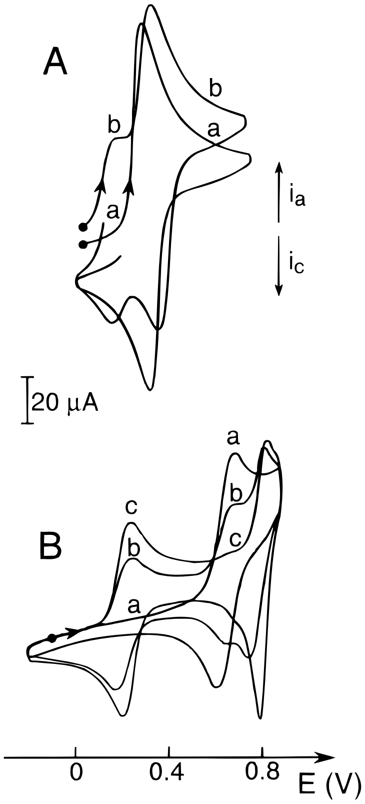

Figure 1. (A) Cyclic voltammograms of L_1 (1.6 mM) in CH_3CN + TBAP 0.1 M: (a) free L_1; (b) L_1 + 0.5 Cu^I. (B) Cyclic voltammograms of L_2 (1.2 mM) in CH_2Cl_2 + TBAP 0.1 M: (a) free L_2; (b) L_2 + 0.5 Cu^I; (c) L_2 + 1 Cu^I. Working electrode, Pt disk (5 mm diameter); scan rate, 0.1 V s^{-1}; E vs Ag/AgNO$_3$, 0.01 M + CH_3CN + TBAP 0.1 M.

our experimental conditions. The working electrode consisted of a platinum disk (5 mm diameter) polished with 2 μm diamond paste. Concentrated stock solutions of $[Cu(CH_3CN)_4](ClO_4)$ and $Cu(ClO_4)_2 \cdot 6H_2O$ in CH_3CN were used for the addition of Cu^I and Cu^{II} cations to electrolytic solution of L_1 and L_2. FAB (positive mode) mass spectra were recorded on an AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd gun using *m*-nitrobenzyl alcohol as matrix. Electrospray MS experiments were performed by the CNRS Microanalysis Laboratory (Lyon, France). ^{1}H NMR spectra were recorded on a Brucker AM 300 spectrometer. UV−visible spectra were obtained on a Varian Cary 1 spectrophotometer. EPR experiments were made with a Brucker ESP 300E spectrometer operating at 9.4 GHz (X band).

Results and Discussion

The cyclic voltammetry (CV) curves for L_1, L_2, and their copper complexes were recorded in CH_3CN or CH_2Cl_2 electrolyte containing 0.1 M TBAP. Their electrochemical data are summarized in Table 1. The CV curves for L_1 and L_2 are characterized by a reversible redox wave corresponding to the regular ferrocene/ferricinium (Fc/Fc$^+$) redox couple at $E_{1/2}$ = 0.33 and 0.56 V in CH_3CN electrolyte, respectively, or 0.45 and 0.69 V in CH_2Cl_2 electrolyte, respectively (Figure 1).

Complexation of L_1 with Cu^I ions causes a gradual positive shift of the Fc/Fc$^+$ wave up to 50 mV, along with the rise of a new redox peaks system ($E_{1/2}$ = 0.19 V in CH_3CN) attributed to the complexed Cu^I/Cu^{II} redox couple. Maximal potential shift of the Fc/Fc$^+$ wave and maximal intensity of the Cu^I/Cu^{II} peaks system are obtained at a Cu^I/L_1 molar ratio equal to 0.5 (Figure 1A, curve b). In contrast, the addition of increasing amounts of Cu^I to an electrolytic solution of L_2 results in a Fc/Fc$^+$ two-wave behavior, i.e. the growth of a new Fc/Fc$^+$ redox wave ($E_{1/2}$ = 0.71 V in CH_3CN and 0.84 V in CH_2Cl_2), which reaches full development after the addition of one molar equivalent of copper salt, at the expense of the original wave for free L_2 (Figure 1B). Strong adsorption phenomena due to solvation effects in CH_2Cl_2 are responsible for a distorted wave for the oxidized, highly charged $[L_2^+ + Cu^{2+}]$ complex. Furthermore, the Cu^I/Cu^{II} redox peaks system for the L_2 complex grows at a more negative potential ($E_{1/2}$ = 0.10 V in CH_3CN and 0.23 V in CH_2Cl_2) compared to L_1. The positive potential shift observed for the Fc/Fc$^+$ redox wave upon complexation of L_1 and L_2 by copper cations can be due to electrostatic repulsion effect between the bound metal cation and the electrogenerated positive charge on the oxidized ferrocenyl subunit. This leads to a decrease of the association constant, K_+, with the oxidized ligand and to a destabilization of the complex.[7] Thus, $\Delta E_{1/2}$ reflects the balance of the interactions of the metal cation between the neutral and the oxidized, charged ligand. The remarkable electrochemical behavior of L_2, in terms of the type (two-wave behavior) of potential shift, can be linked to a high binding constant, K, with the neutral ligand in association with a large K/K_+ ratio.[8] It may also, in part, be due to a structural effect leading to a noncoplanarity of the Cp rings in the complex, which is known to cause an important positive potential shift in complexed[7,9] or strained bridged[10] ferrocenophanes. It must be emphasized that such two-wave feature allows the amperometric recognition and titration of the guest cation.

The relatively high Cu^I/Cu^{II} redox potentials for complexes with L_1 and L_2 are in good agreement with those previously reported for various polypyridyl complexes.[11] Rotating-disk voltammetry experiments have confirmed that one Cu^I ion is complexed with two L_1 and one L_2 ligands respectively, as evaluated from the comparison of the heights of Cu^I/Cu^{II} and Fc/Fc$^+$ oxidation waves. This stoichiometry is corroborated by ^{1}H NMR (vide supra) and MS data. In addition, both complexes are characterized by a broad, irreversible reduction peak around −1.3 V corresponding to dissociation and coating of the electrode by copper metal. Identical results, i.e. superposable CV curves and same potentials for both complexed Cu^I/Cu^{II} and Fc/Fc$^+$ redox couples, were obtained following the addition of Cu^{II} instead of Cu^I. Since copper(I) oxidation occurs before

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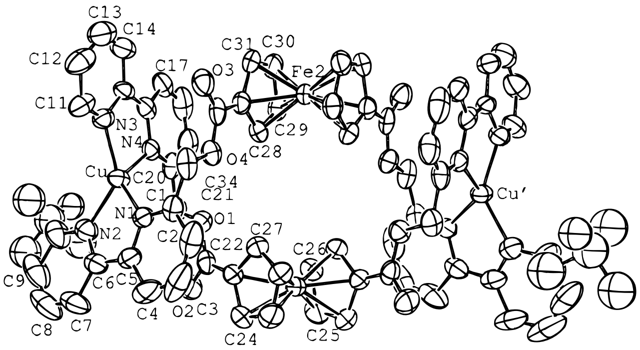

Figure 2. X-ray structure of the $[Cu^I_2(\mathbf{L_2})_2](BF_4)_2$ complex.

ferrocene oxidation, it must be emphasized that the redox potential of the complexed Fc/Fc^+ couple determined from CV curves is always that for a complex in its Cu^{II} form.

The addition of Cu^I cations in solutions of $\mathbf{L_1}$ and $\mathbf{L_2}$ produces significant perturbations of all ^1H NMR resonances recorded at 273 K in CD_2Cl_2. Signals for both free and complexed ligands are observed at a substoichiometry of copper salt. This fact reveals the inertness of these complexes, i.e. intermolecular exchange is restricted on the NMR time scale. In the $\mathbf{L_2} + Cu^I$ complex, most of the resonances of protons at the 2,2′-bipyridine rings are shifted downfield. The most characteristic changes of signals are observed in the ferrocene and in the methylene protons adjacent to the bipyridyl groups. As already noticed in the copper complex of another 1,1′-(bispyridyl)ferrocene,[3c] ferrocene protons pairs become nonequivalent; in particular, the α′-Cp resonances at 4.90 ppm in the free ligand are shifted upfield up to 4.73 ppm, whereas the α-Cp signal is found at 3.68 ppm. The NMR signals of the methylene protons change from a singlet (5.39 ppm in free $\mathbf{L_2}$) to an AB system (exo-H: 5.62 ppm, $J = 11.7$ Hz; endo-H: 4.60 ppm, $J = 11.7$ Hz). This AB pattern was clearly observed even at room temperature. The prochirality of the methylene protons is consistent with rigidification of the 2,2′-bipyridyl arms due to the coordination to the metal center.

The crystal structure of complex formed between $\mathbf{L_2}$ and Cu^I (Figure 2) reveals that it indeed forms a 2:2 ($\mathbf{L_2}$:Cu) coordination stoichiometry, to arrange a pseudotetrahedral coordination geometry around the metal. The solid state is best described as a double-stranded helix with the two copper(I) cations lying at a center-to-center separation of 11.54 Å. The four coplanar metals form a slightly distorted rhombus with sides of 6.48 and 6.60 Å and interior angles of 56.06 and 125.90°. The two iron centers lie on the imposed C_2 axis of the molecule at a distance of 6.15 Å. Each ligand wraps around the two copper(I) cations, with the two bipy fragments belonging to the same metallosynthon being twisted by ca. 176°. Each copper(I) cation has distorted tetrahedral coordination with a small angle of ca. 82° and a wide angle of 131°. The copper cation is symmetrically coordinated to four nitrogen atoms (average distance of 2.02 Å) and there is no indication for a copper(I) oxygen interaction (>3.3 Å). The bipy chelates are slightly twisted about the exocyclic central C−C bond (6.44 and 12.34° respectively for the bipy on the bottom and top of Figure 2). The ester groups are almost coplanar with the Cp rings (tilted angle of ca. 1.6°) while exhibiting a twisted angle of 75.46−66.57° with the bipy subunits. No significant deformation of the almost parallel Cp rings is observed. Both tetrafluoroborate anions lie outside the macrocyclic cavity.

Although an X-ray structural determination of the $Cu^{II} + \mathbf{L_2}$ complex remains elusive, it was shown by EPR experiments performed in frozen DMSO that this complex and its $\mathbf{L_1}$ analogue, present the usual line shape for mononuclear Cu^{II} complexes with a $d_{x^2-y^2}$ ground state and $g_{\|} > g_{\perp} > 2.03$ indicating an axial geometry. It has been suggested that the $g_{\|}/A_{\|}$ ratio gives an indication of the stereochemistry of such complexes.[12] The value of 182 cm for $\mathbf{L_1} + Cu^{II}$ complex indicates a strong tetrahedral distortion, while the value of 151 cm for $\mathbf{L_2} + Cu^{II}$ complex is in agreement with only a slight tetrahedral distortion from tetragonal geometry.

While the solid-state structure of the $\mathbf{L_2} + Cu^I$ complex is unambiguously of 2:2 stoichiometry, evidence for a fast dissociation upon dissolution to give a 1:1 complex was obtained from additional experiments. First, no change in the $E_{1/2}$ and in the reversibility of the Cu^I/Cu^{II} and Fc/Fc^+ redox couples has been observed in the 5×10^{-2} M (saturated electrolytic solution, prepared from the isolated complex) to 10^{-5} M concentration range, demonstrating that no change occurs in the stoichiometry of the dissolved complex. It is expected that an interconversion from a 2:2 to a 1:1 coordination stoichiometry upon switching the oxidation state of the Cu cation would result in irreversible electrochemical features and different redox systems for the $\mathbf{L_2}$ + Cu and 2 $\mathbf{L_2}$ + Cu complexes, as already demonstrated for monomer−dimer interconversion in related Cu-oligopyridine complexes.[13] Furthermore, the copper(II) complex of $\mathbf{L_2}$ could either be prepared by mixing $\mathbf{L_2}$ with cupric salts or by chemical oxidation of the cuprous complex with Ce(IV) in acidic acetonitrile or by potentiostatic electrolysis of an electrolytic acetonitrile solution of the cuprous complex at ca. 0.4 V. During chemical oxidation, no intermediate in the time scale of 1 ms could be observed by stopped-flow experiments emphasizing the fact that the dimeric copper(I) complex do not survive in solution. Based also on ES-MS data,[14] it is concluded that the Cu^I and Cu^{II} complexes with $\mathbf{L_2}$ are 1:1 species in solution. Close examination of CPK molecular models clearly show that the 1:1 assembly is a possible structure for the $\mathbf{L_2}$ + Cu complexes.

Owing to the remarkable electrochemical recognition properties of this new ferrocene-2,2′-bipyridine ligands, work is in progress to immobilize these redox receptors with the aim to construct novel electroactive chemical sensors.

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Supporting Information Available: Complete tables of crystal data and structure refinement, fractional atomic coordinates, thermal parameters, and bond lengths and angles and a figure showing ^1H NMR spectra (CD_2Cl_2, 273 K) of free $\mathbf{L_2}$ and of the isolated Cu^I complex are available (15 pages). Ordering instructions are given on any current masthead page.

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(14) No significant peaks were observed at (i) 674 m/z ($z = 2$) for $[Cu^I_2(\mathbf{L_2})_2]^{2+}$ or 1447 m/z ($z = 1$) for $\{[Cu^I_2(\mathbf{L_2})_2]^{2+}, ClO_4^-\}$ for the copper(I) complex or (ii) 337 m/z ($z = 4$) for $[Cu^{II}_2(\mathbf{L_2})_2]^{4+}$, 482 m/z ($z = 3$) for $\{[Cu^{II}_2(\mathbf{L_2})_2]^{4+}, ClO_4^-\}$, 773 m/z ($z = 2$) for $\{[Cu^{II}_2(\mathbf{L_2})_2]^{4+}, 2ClO_4^-\}$, or 1645 m/z ($z = 1$) for $\{[Cu^{II}_2(\mathbf{L_2})_2]^{4+}, 3ClO_4^-\}$ for the copper(II) complex.