Synthesis and Properties of Silver(I) and Copper(I) Helicates with Imine-Bridged Oligobipyridine Ligands

Regine Stiller[+] and Jean-Marie Lehn*

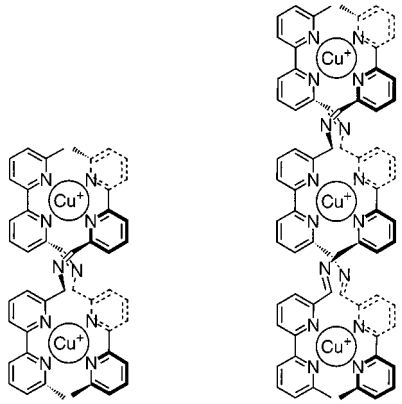
Institut Le Bel, Université Louis Pasteur,
4, rue Blaise Pascal, F-67000 Strasbourg, France

Received February 12, 1998

Keywords: Helicates / Oligobipyridine ligands / Self-recognition / NMR titration / Self-assembly

Oligobipyridine ligands containing one or two imine bridges were found to form double helicates by treatment with copper(I) or silver(I). The properties of the complexes are similar to those of oxapropylene-bridged oligobipyridines. Titration of a mixture of the bis(bipyridine) and the tris(bipyridine) ligands with silver(I) hexafluorophosphate showed that helicates formed with strict self-recognition.

In recent years, the design and study of properties of double and triple helical complexes organized by self-assembly of two or three ligand strands and metal ions to the so-called helicates have been subject to detailed investigations.[1][2][3][4][5][6][7][8] The architectural information is found in the matching between the ligand binding sites and the stereochemical preferences of the metal ion. Complexation of oligo-bidentate strands with tetrahedrally or octahedrally coordinating ions leads respectively to double or triple helices[1][2][3][4][5][][7][8][9]. On the other hand, oligotridentate strands give double or triple helices with octahedrally or nine coordinated ions[2][3][10][11]. The helicate formation with oligobipyridine ligands was found to occur with positive cooperativity[12], self-recognition and self/non-self-discrimination.[1][9] In the case of oligobipyridine ligands, spacers are introduced which separate the different metal-binding centers and dispose them in a suitable way for formation of multinuclear complexes. The features (length, flexibility, constitution) of the spacer separating the 2,2′-bipyridines (bpy) should be such as to allow the helical arrangement around metal ions but hinder the coordination of several binding units to the same metal ion by back-folding of the strand. Several spacers have been tested so far, of which the oxapropylene bridge (CH_2-O-CH_2) was the most studied.[1][2][5] The analogous bridge (CH_2-S-CH_2) did not allow helicate formation perhaps due to the competition of sulfur for Cu^I binding.[13] The ethylene bridge (CH_2-CH_2) permits helicate formation with Cu^I[14][15] whereas the unsaturated bridge (CH=CH) does not because of its rigidity.[16] In continuation of these studies, we report here on the syntheses of two novel oligobipyridine strands **1** and **2** with imine bridges. These ligands contain a rigid double bond and a nitrogen atom as potentially competing binding site, so that it has first to be shown whether helicate formation does occur. This −CH=N− bridge can easily be formed from monomer bpy units bearing amine and aldehyde functional groups in a reversible reaction, thus opening the way to the design of a system which might display self-generation and self-replicating properties.



1-H **2-H**

Synthesis of the Oligobipyridine Ligands 1 and 2

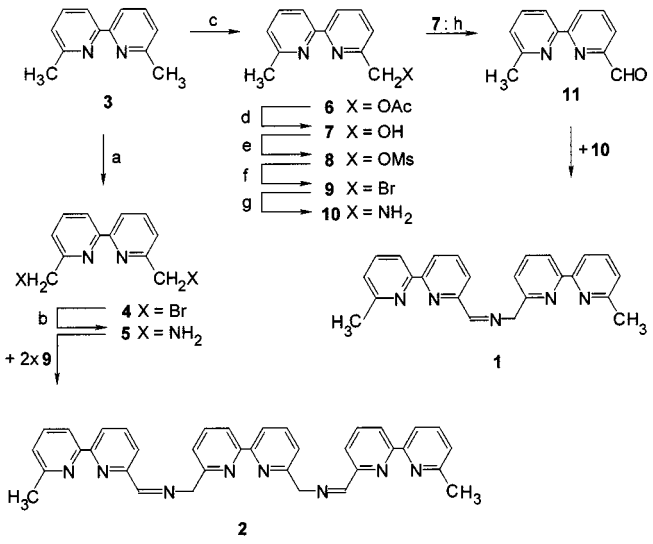
The synthetic precursors for the formation of ligands **1** and **2** were all obtained from 6,6′-dimethyl-2,2′-bipyridine **3** (Scheme 1). After radical NBS bromination to **4** followed by amination with hexamethylene tetramine[17][18] the symmetrical diamine **5** was obtained. For the monosubstituted precursors **10** and **11**, another strategy proved to be more practical. Compound **3** was unsymmetrically functionalized by *N*-oxidation with *meta*-chloroperbenzoic acid[19] followed by rearrangement to acetate **6** and hydrolysis to monoalcohol **7**, which, after activation as monomesylate **8**, was converted into monobromide **9**.[5] The monobromide **9** was then converted into the monoamine **10** with hexamethylene tetramine. Alcohol **7** was also oxidized to monoaldehyde **11** under Swern conditions. The ligand synthesis was completed by Schiff base formation between the

[+] Present address: Biochemisches Institut der Universität Kiel, Olshausenstr. 40, D-24098 Kiel.

  1434−1948/98/0707−0977 $ 17.50+.50/0

monoaldehyde **11** and either monoamine **10** or diamine **5** to form the dimer **1** or the trimer **2**, respectively.

Scheme 1. Synthesis of the oligobipyridine ligands **1** and **2**



Formation of the Helicates 1-H and 2-H with Ag^I

The helicate complexes of ligands **1** and **2** were formed in situ by stoichiometric addition of the Ag^I salt to the ligands dissolved in CD_2Cl_2 with a minimal amount of CD_3CN. Their helical structure was proved by 500-MHz NMR and 2-dimensional H,H-correlated ^{1}H-NMR spectroscopy (COSY). In line with earlier observations[1][5] helicate formation results in characteristic changes in the NMR spectrum compared to that of the free ligands **1** and **2**. Shifts to lower δ values are observed for the methylene, imine, and methyl protons in the range of $\delta = 0.6-0.8$. As a result of helicate formation, the singlet for the methylene protons of the free ligand is split into an AB system ($J \approx 18$ Hz) because these protons are no longer equivalent in the complex. Furthermore, the singlet for the imine proton is also shifted to smaller δ values and now overlaps with the signals of the aromatic ring protons (compare Figure 3).

The self-assembly of the silver(I) helicates **1-H** and **2-H** was investigated by NMR titration experiments, which were performed by progressively adding a solution of $AgPF_6$ in CD_2Cl_2/CD_3CN (1:1) to a solution of the ligand in CD_2Cl_2 (spectra not shown, compare Figure 3). For trimer **2**, the following changes in the NMR spectrum were observed. Immediately after addition of only 0.28 equiv. of Ag^I with respect to binding sites, the A_2 system of the methylene protons splits into an AB system typical for helicity. Also, the aromatic peaks are significantly shifted up-field. With further addition of Ag^I, the AB pattern is still present, and even with an excess of Ag^I the helix is not destroyed. The dimer helicate is not as stable as the trimer helicate. Titrations of dimer **1** with $AgPF_6$ solution show that in the range of 0.2−0.9 equiv. of Ag^I added, the spectrum only consists of broad signals resulting from fast exchanges. The AB system only appears after addition of exactly one equiv. of Ag^I. On further titration, this signal rapidly converges into an A_2 signal which is shifted upfield (ca 0.7 ppm) compared to the free ligand, indicating that a species different from the helicate or the free ligand is formed. These observations can be explained by dissociation of the helicate structure and fast ligand exchange with the complex(es) formed. This agrees with the following observations: (1) in the new species, the methylene protons give again only an A_2 signal; (2) the imine proton is no longer shielded by the pyridine rings of the second strand, indeed a singlet at $\delta = 8.35$ appears which can be assigned to the imine proton; (3) on further addition of Ag^I the spectrum does not change.

Spectral and Thermodynamic Properties of the Copper(I) Helicates

The UV spectra of the colorless ligands **1** and **2** in dichloromethane as well as their monomers **5**, **10**, and **11** display two intense absorptions around 240 nm and 300 nm attributed to $\pi_2 \rightarrow \pi^*$ and $\pi_1 \rightarrow \pi^*$ by comparison with 2,2′-bipyridine.[20] Upon complexation with Cu^I ions, the $\pi_2 \rightarrow \pi^*$ band is split into several bands and the $\pi_1 \rightarrow \pi^*$ band is slightly red-shifted. Most significant is the appearance of a new band near 450 nm, which is responsible for the red color of the complexes. It can be assigned to MLCT ($Cu^I \rightarrow \pi^*$) transitions typical for pseudotetrahedral $[Cu(a,a'\text{-diimine})_2]^+$ chromophores.[21]

Figure 1. UV spectra for the titration of the bis(bipyridine) ligand **1** with $[Cu(CH_3CN)_4](PF_6)$ in dichloromethane; the amount of salt added increases from 1 to 19

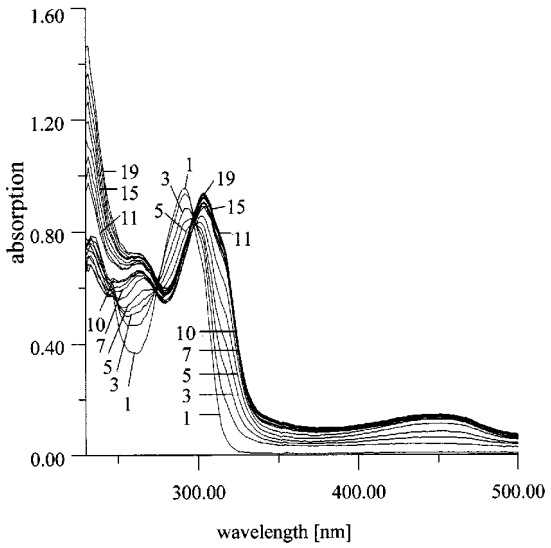


Figure 1 displays the UV spectra of the titration of dimer **1** with $[Cu(CH_3CN)_4](PF_6)$. Two isosbestic points can be distinguished at 299 nm and 273 nm. This indicates that either only two main products exist in solution or that eventual intermediates have the same molar extinction coefficient ε. With increasing Cu^I concentration, the bands for the $\pi \rightarrow \pi^*$ transitions are red-shifted because of complex formation. The absorbance diagram (not shown) for the MLCT band indicates that the final level is reached at a

ratio $c_M/c_L = 1$, which corresponds to equivalency for helicate formation.

The data obtained from the titration spectra were used for the determination of the binding constants with the LETAGROP-SPEFO program.[12a] This program allows the calculation of the binding constants β_{ml} for each species M_mL_l of a proposed model in a non-linear best fit of spectrophotometric data. For the dimer, the following equilibria should be considered:

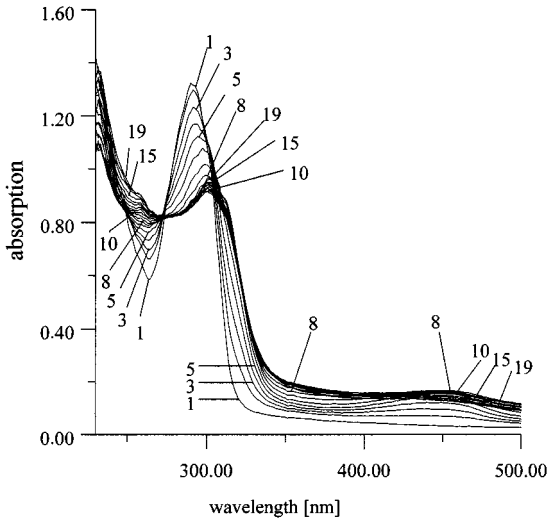
$$M + L \rightleftharpoons ML$$
$$ML + L \rightleftharpoons ML_2$$
$$ML_2 + M \rightleftharpoons M_2L_2$$

The first equilibrium was neglected as its inclusion did not yield satisfactory results. This is reasonable since the formation of a 1:1 complex is unlikely for steric reasons. The log β_{ml} values calculated are in good agreement with those determined for a 4,4′-substituted dimer:[22]

$$\log \beta_{12} = 9.1 \qquad M + 2\,L \rightleftharpoons ML_2$$
$$\log \beta_{22} = 13.05 \qquad 2\,M + 2\,L \rightleftharpoons M_2L_2$$

Titration spectra for the trimer **2** are given in Figure 2. An isosbestic point is found at 273 nm. It should be noted that the absorbance at 450 nm first increases with the concentration of Cu^I as the trimer helicate is formed, but with an excess of more than 1.35 equiv. of Cu^I, it sinks again indicating the destruction of the helicate. This differs from the results obtained for NMR titrations with Ag^I (see above) and may be related to the higher stability of Cu^I versus Ag^I helicates. The ε value of the $\pi_1 \rightarrow \pi^*$ transition decreases much more than in the case of the dimer, and a shoulder develops at 313 nm.

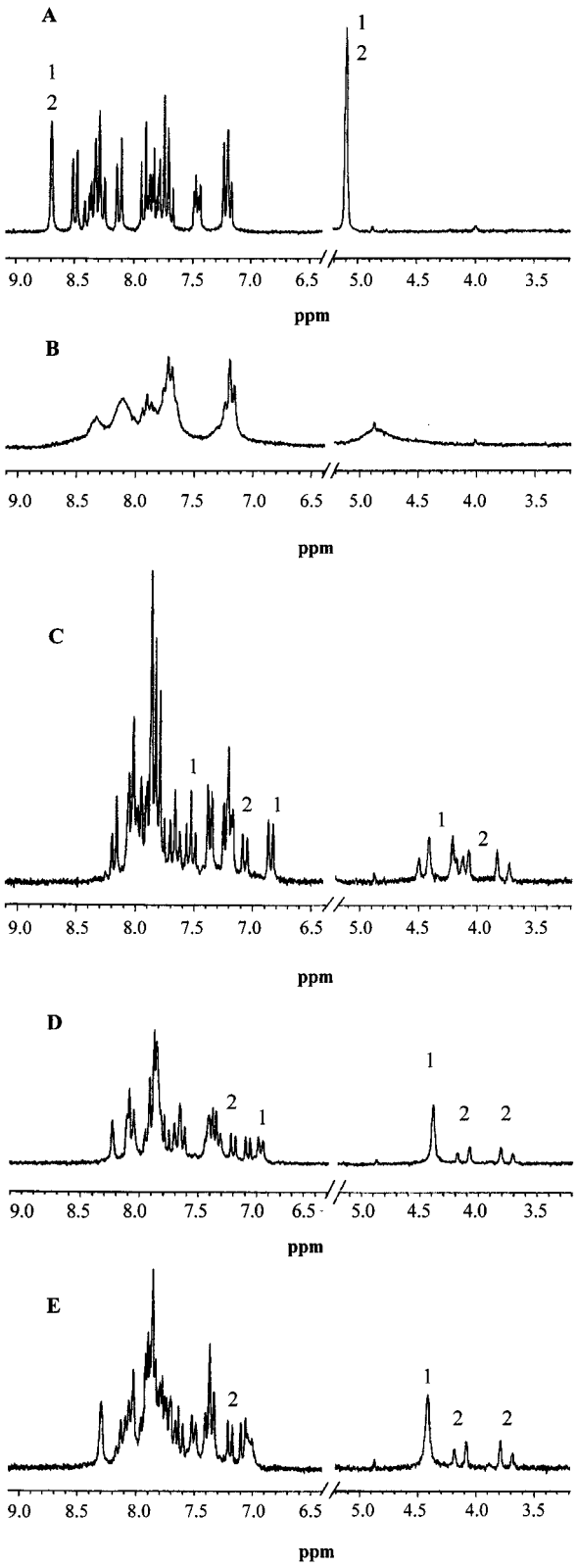
Figure 2. UV spectra for the titration of the tris(bipyridine) ligand **2** with $[Cu(CH_3CN)_4](PF_6)$ in dichloromethane; the amount of salt added increases from 1 to 19



Self-Recognition in the Self-Assembly of the Helicates 1-H and 2-H

It has been found earlier that helicate formation from mixtures of oligobipyridine ligands occurs with self-recog-

Figure 3. 200-MHz ^{1}H-NMR spectra for the titration of ligands **1** and **2** in CD_2Cl_2 with $AgPF_6$ in CD_2Cl_2/CD_3CN (1:1); signals ascribed to the dimer are identified by **1**, those of the trimer by **2**; the following equivalents of Ag^I were added: A−E: 0, 0.2, 0.61, 0.75, 1 equiv. with respect to bipyridine binding sites



nition, each strand assembling with an identical partner.[9] In order to investigate whether this was also the case with the present ligands **1** and **2**, we performed a competition experiment by titrating mixtures of the two compounds. In a vernier mechanism[9][23], two complementary components differing in length aggregate to give linear side-by-side adducts; growth may then continue until the tips of the adjacent aggregates are in register. According to this model, an aggregate of 2 trimers, 3 dimers, and 6 Ag^I ions would form, whereas self-recognition of identical ligands leads to two individual helicate species. A mixture of 1.5 equiv. of dimer **1** and 1 equiv. of trimer **2** in CD_2Cl_2 was titrated with a solution of $AgPF_6$ in CD_2Cl_2/CD_3CN (1:1) and the titration was followed by recording the 200-MHz ^{1}H-NMR spectra (Figure 3). In agreement with titrations of the individual ligands, the singlet for the methylene protons collapsed to a broad signal immediately after addition of Ag^I. At low salt concentration, all signals were broad and badly resolved due to fast exchange. After addition of ca. 0.5 equiv. Ag^I per binding site, helicate formation can be anticipated, and indeed with 0.6 equiv. Ag^I added, two individual AB systems corresponding to the dimer and trimer helicates were clearly resolved. These titration NMR spectra (Figure 3) combine the features of the individual titration spectra indicating strict self-recognition as no new species are found. A polymer resulting from the vernier mechanism would be destabilised by steric interaction in the center of the structure between the methyl groups. On the other hand, its formation is entropically disfavored as the number of particles formed is smaller than in the case of a mixture of helicates. This agrees with the previous results where self-recognition in helicate formation with (CH_2-O-CH_2)-bridged oligobipyridine ligands was observed.[9] The ability to form helicates as well as to perform self-recognition make imine-bridged oligobipyridine strands potential candidates for setting up systems displaying self-generation and self-replication processes.[29]

We thank the *Alexander von Humboldt Stiftung* for a *Feodor Lynen* stipend to R. S. as well as the *CNRS* (URA422) and the *College de France* for financial support. We are also grateful to Dr. *Annie Marquis* for her help in some experiments and measurements and for the binding constants computations.

Experimental Section

General: All solvents were freshly distilled: chloroform from $CaCl_2$; acetonitrile and DMSO from CaH_2; dichloromethane, CCl_4 and TEA from P_2O_5; toluene from Na; THF from Na/benzophenone. Ethyl acetate and solvents used for imine syntheses and UV experiments were filtered through basic alumina before use. Reagents were used without further purification unless otherwise noted. $AgPF_6$ was obtained from Merck. $[Cu(CH_3CN)_4]PF_6$, $[Cu(CH_3CN)_4]BF_4$ and $[Cu(CH_3CN)_4]ClO_4$ were prepared according to a literature procedure.[24] − M.p. (uncorrected): Digital melting-point apparatus (Electrothermal). − UV/Vis: Cary 13 spectrometer. − NMR: Bruker AC-200 and Bruker ARX 500; chemical shifts in ppm rel. to TMS ($\delta = 0$). − 6-Bromo-2-picoline[25], 6,6′-dimethyl-2,2′-bipyridine[26] (**3**), 6,6′-bis(bromomethyl)-2,2′-bipyridine (**4**)[27], 6,6′-bis(aminomethyl)-2,2′-bipyridine (**5**)[18], 6-(hydroxymethyl)-6′-methyl-2,2′-bipyridine (**7**)[19], 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**9**)[28] were prepared according to literature procedures. Crude monoalcohol **7** was further purified by chromatography [alumina; A: dichloromethane; B: dichloromethane/2% methanol; elution procedure: 700 ml of A, followed by 400 ml of A/B (3:1), followed by 300 ml of A/B (2:1)]. In some cases, crude **7** was partitioned between water (pH = 2−3) and chloroform/hexane (1:1). The water phase containing **7** was neutralized with $NaHCO_3$ and extracted with chloroform. The organic layer was then dried with Na_2SO_4 and concentrated.

Bis(bipyridine) Ligand **1**: 30 mg (0.15 mmol) of monoamine **10** was suspended in 1 ml of acetonitrile. A solution of 30 mg (0.15 mmol) of monoaldehyde **11** in 1 ml of acetonitrile was added slowly. Immediately, a white precipitate formed. The mixture was stirred at room temp. under argon for 2 h. The white precipitate was centrifuged off, washed with acetonitrile, again centrifuged, and dried under vacuum yielding 46 mg of **1** (0.12 mmol, 80%) as a white solid, m.p. 181−182°C. − $C_{24}H_{21}N_5$ (379.18): calcd. C 75.97, H 5.58, N 18.46; found C 76.22, H 5.83. − FAB-MS: *m/z* calcd. for M^+: 379.18; found for MH^+: 380.1; EI-MS: M^+: 379.2. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.69 (s, 1 H, imine-*H*), 8.48 (d, 1 H, aromatic-3^{II}), 8.33 (d, 1 H, aromatic-3^{III}), 8.30 (d, 1 H, aromatic-3^{I}), 8.26 (d, 1 H, aromatic-3^{IV}) 8.11 (d, 1 H, aromatic-5^{II}), 7.89 (t, 1 H, aromatic-4^{II}), 7.82 (t, 1 H, aromatic-4^{III}), 7.73 (t, 1 H, aromatic-4^{I}), 7.70 (t, 1 H, aromatic-4^{IV}), 7.44 (d, 1 H, aromatic-5^{III}), 7.21 (d, 1 H, aromatic-5^{I}), 7.18 (d, 1 H, aromatic-5^{IV}), 5.09 (s, 2 H, C*H*$_2$), 2.61 (s, 3 H, C*H*$_3$), 2.60 (s, 3 H, C*H*′$_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 164.64 (imine-*C*), 158.38, 158.11, 157.95, 156.30, 156.12, 155.27, 154.13, (8 C-C); 137.55, 137.49, 137.21, 137.11, 123.55, 123.29, 122.41, 122.16, 121.02, 119.62, 118.40, 118.26 (12 *C*-H); 66.78 (*C*H$_2$); 24.76 (*C*H$_3$). − UV/Vis dichloromethane/acetonitrile (2:1)]: λ_{max} (lg ε) = 290 nm (4.55), 233 (4.46); shoulder (lg ε) = 301 nm (4.41), 246 nm (4.30).

Tris(bipyridine) Ligand **2**: 50 mg (0.23 mmol) of diamine **5** was suspended in 2 ml of acetonitrile. A solution of 93 mg (0.47 mmol) of monoaldehyde **11**, dissolved in 3 ml of acetonitrile, was added. The mixture was stirred for 2 h under argon at room temp. The white precipitate was centrifuged off, washed with acetonitrile, again centrifuged and dried under vacuum yielding 96 mg of **2** (0.17 mmol, 72%) as a white solid, m.p. 186−188°C. − $C_{36}H_{30}N_8$ (574.69): calcd. C 75.24, H 5.26, N 19.50; found C 74.21, H 5.25, N 19.50. − FAB-MS: *m/z* calcd. for M^+: 574.3; found for MH^+: 575.1. − ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.70 (s, 2 H, imine-*H*), 8.49 (dd, 2 H, aromatic-3^{II}), 8.39 (d, 2 H, aromatic-3^{III}), 8.31 (d, 2 H, aromatic-3^{I}), 8.12 (dd, 2 H, aromatic-5^{II}), 7.90 (t, 2 H, aromatic-4^{II}), 7.84 (t, 2 H, aromatic-4^{III}), 7.74 (t, 2 H, aromatic-4^{I}), 7.47 (d, 2 H, aromatic-5^{III}), 7.21 (d, 2 H, aromatic-5^{I}), 5.11 (d, 4 H, C*H*$_2$), 2.62 (s, 6 H, C*H*$_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 164.67 (imine-*C*), 158.34 (C-C), 137.49, 137.18, 123.52, 122.41, 122.29, 121.00, 119.72, 118.25 (C-H), 66.74 (*C*H$_2$), 24.72 (*C*H$_3$). UV/Vis (dichloromethane): λ_{max} (lg ε) = 291 nm (4.68); shoulder (lg ε) = 303 nm (4.55), 247 (4.50).

6-Aminomethyl-6′-methyl-2,2′-bipyridine (**10**): 0.81 g (5.8 mmol) of hexamethylenetetramine was stirred at 40°C in 12 ml of chloroform until everything was dissolved. A solution of 1.32 g (5.6 mmol) of 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**9**) in 10 ml of chloroform was added slowly. A white precipitate formed immediately. The addition funnel was washed with 3 ml of chloroform and the mixture was refluxed for 2 h. After cooling to room temp., the precipitate was filtered and dried. The solid was refluxed for 2 h at 70°C with a mixture of 11 ml of ethanol, 1.5 ml of water, and 1.5 ml of conc. HCl. The solution was left in a refrigerator overnight. The precipitate was filtered off, the filtrate was concentrated

to give more precipitate. The solids were dried under vacuum, redissolved in a minimal amount of water and adjusted to pH = 13 with 6 N NaOH. The water phase was extracted with dichloromethane (3 × 50 ml), the organic phase was dried with Na_2SO_4, concentrated and dried under vacuum yielding 0.33 g **10** (1.7 mmol, 30%) as a yellow solid. − TLC (Al_2O_3; dichloromethane/2% methanol): R_f = 0.10. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.28 (d, 1 H, aromatic H), 8.24 (d, 1 H, aromatic H), 7.76 (t, 1 H, aromatic H), 7.69 (t, 1 H, aromatic H), 7.25 (d, 1 H, aromatic H) 7.16 (d, 1 H, aromatic H), 4.04 (s, 2 H, CH_2), 2.63 (s, 3 H, CH_3), 1.73 (*s*, NH_2). − UV/Vis (dichloromethane): λ_{max} (lg ε) = 239 nm (4.13), 292 (4.34); shoulder (lg ε) = 245 nm (4.11), 283 (4.27), 301 (4.20).

6-Methyl-2,2′-bipyridine-6′-carbaldehyde (**11**): A solution of 2.5 ml of freshly distilled oxalyl chloride in 30 ml of dichloromethane was cooled to −60°C. A mixture of 1.5 ml of DMSO in 6 ml of dichloromethane was added in 10 min and it was stirred for another 10 min at −60°C. A solution of 1.48 g of highly purified 6-hydroxymethyl-6′-methyl-2,2′-bipyridine (**7**) in 12 ml of dichloromethane was added slowly, keeping the temperature at −60°C. The mixture was stirred for 30 min at that temperature. Then, 7.5 ml of TEA was added slowly. After the addition was complete, the mixture was warmed up to room temp. and 30 min later 60 ml of water was added. The organic phase was separated and the water was extracted with dichloromethane (2 × 40 ml). The combined organic phases were washed with 50 ml of brine, dried with Na_2SO_4, and concentrated. The residue was chromatographed [silica gel (2 × 14 cm); A: dichloromethane; B: dichloromethane/2% TEA/2% methanol; elution procedure: 300 ml of A followed by 200 ml of A/B (9:1)]. Recrystallization from ethanol gave 0.31 g of **11** (1.56 mmol, 21%), cream colored solid, m.p. 135−136°C. − TLC (Al_2O_3; dichloromethane/1% methanol): R_f = 0.66. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.16 (s, 1 H, C*H*O), 8.68 (dd, 1 H, aromatic H), 8.34 (d, 1 H, aromatic H), 7.98 (m, 2 H, aromatic H), 7.75 (t, 1 H, aromatic H), 7.22 (d, 1 H, aromatic H), 2.66 (s, 3 H, CH_3). − UV/Vis (dichloromethane): λ_{max} (lg ε) = 287 nm (4.08), 229 (4.15); shoulder (lg ε) = 299 nm (3.92), 253 (3.86).

General Procedure for the Preparation of the Helicate Complexes: Solvents were freshly distilled and filtered through a column of basic alumina and molcular sieves (4 A) before use. Copper(I) salts and silver(I) salts were dissolved in dichloromethane/acetonitrile (1:1). They were stable in solution for several weeks. Complexes were prepared by mixing a solution of the ligand in dichloromethane and adding the proper amount of salt solution (usually 0.5 equivalents per binding site). The complexes were characterized by UV and NMR.

Complexes of the Bis(bipyridine) Ligand **1**

*[Cu_2(**1**)$_2$](ClO_4)$_2$*: UV/Vis (dichloromethane): λ_{max} (lg ε) = 450 nm (3.81), 302 (4.74), 263 (4.62); shoulder (lg ε) = 317 nm (4.62). − FAB-MS: calcd. for $C_{48}H_{42}ClCu_2N_{10}O_4$: 983.17; found for $\{[Cu_2(\mathbf{1})_2](ClO_4)\}^+$: 985.2. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.55 (d, 1 H, aromatic H), 8.47 (d, 1 H, aromatic H), 8.41 (d, 1 H, aromatic H), 8.24 (d, 1 H, aromatic H), 8.19 (t, 1 H, aromatic H), 8.08 (t, 1 H, aromatic H), 7.96 (t, 1 H, aromatic H), 7.62 (m, 2 H, aromatic H), 7.49 (t, 1 H, aromatic H), 7.36 (d, 1 H, aromatic H), 6.90 (d, 1 H, aromatic H), 4.57 (dd, 1 H, CH_2), 4.32 (dd, 1 H, CH'_2), 2.15 (s, 3 H, CH_3), 1.88 (s, 3 H, CH'_3).

*[Cu_2(**1**)$_2$](PF_6)$_2$*: UV/Vis (dichloromethane): λ_{max} (lg ε) = 451 nm (4.01), 301 (4.84), 267 (4.68), 231 (4.77); shoulder (lg ε) = 317 nm (4.66).

*[Ag_2(**1**)$_2$](PF_6)$_2$*: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.19 (d, 1 H, aromatic-3^{IV}), 8.01 (s, 1 H, imine-*H*), ca. 8.01 (t, 1 H, aromatic-4^{IV}), 7.99 (d, 1 H, aromatic-3^{I}), ca. 7.90 (d, 1 H, aromatic-3^{II}), ca. 7.87 (t, 1 H, aromatic-4^{II}), ca. 7.82 (d, 1 H, aromatic-3^{III}), ca. 7.81 (t, 1 H, aromatic-4^{I}), 7.52 (t, 1 H, aromatic-4^{III}), 7.36 (d, 1 H, aromatic-5^{II}), 7.21 (d, 1 H, aromatic-5^{I}), 7.16 (d, 1 H, aromatic-5^{IV}), 6.84 (d, 1 H, aromatic-5^{III}), 4.46 (d, 1 H, CH_2), 4.17 (d, 1 H, CH'_2), 2.33 (s, 6 H, CH_3). − FAB-MS: calcd. for $[Ag_2(\mathbf{1})_2](PF_6)^+$: 1117.1; found: 1118.7; calcd. for $[Ag_2(\mathbf{1})_2]^{2+}$: 972.1; found: 973.8.

*[Ag_2(**1**)$_2$](*Tf*)$_2$*: ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.20 (d, 1 H, aromatic-3^{IV}), ca. 8.01 (m, 3 H, aromatic H/imine-*H*), ca. 7.87 (m, 4 H, aromatic H), 7.52 (t, 1 H, aromatic-4^{III}), 7.42 (d, 1 H, aromatic-5^{II}), 7.20 (d, 1 H, aromatic-5^{I}), 7.15 (d, 1 H, aromatic-5^{IV}), 6.84 (d, 1 H, aromatic-5^{III}), 4.47 (d, 1 H, CH_2), 4.15 (d, 1 H, CH'_2), 2.34 (s, 6 H, CH_3).

Complexes of the Tris(bipyridine) Ligand **2**

*[Cu_3(**2**)$_2$](ClO_4)$_3$*: UV/Vis (dichloromethane): λ_{max} (lg ε) = 450 nm (3.78), 302 (4.71); shoulder (lg ε) = 313 nm (4.66), 260 (4.68). − FAB-MS: calcd. for M^+ ($C_{72}H_{60}Cl_3Cu_3N_{16}O_8$): 1634.15; found 1638.2. − ^{1}H NMR [200 MHz, CD_2Cl_2/CD_3CN (1:1)]: δ = ca. 8.49 (d, aromatic H), ca. 8.14 (m, aromatic H), ca. 8.00 (m, aromatic H), ca. 7.88 (m, aromatic H), 7.62 (t, aromatic H) 7.51 (m, aromatic H), 7.32 (t, aromatic H), 7.16 (d, aromatic H), 7.00 (d, aromatic H), 6.81 (d, aromatic H), 4.12 (d, CH_2), 3.98 (d, CH'_2), 1.95 (s, CH_3).

*[Cu_3(**2**)$_2$](PF_6)$_3$*: UV/Vis (dichloromethane): λ_{max} (lg ε) = 451 nm (4.03)ł 302 (4.80), 231 (4.87); shoulder (lg ε) = 313 nm (4.75), 260 (4.74).

*[Ag_3(**2**)$_2$](PF_6)$_3$*: ^{1}H NMR (500 MHz, CD_2Cl_2): 8.07 (d, 1 H, aromatic-3^{I}), 7.93 (s, 1 H, imine-*H*), ca. 7.88 (t, 1 H, aromatic-4^{I}), 7.86 (d, 1 H, aromatic-3^{II}), 7.65 (t, 1 H, aromatic-4^{II}), ca. 7.61 (d, 1 H, aromatic-3^{III}), 7.47 (t, 1 H, aromatic-4^{III}), 7.13 (d, 1 H, aromatic-5^{II}), 7.02 (d, 1 H, aromatic-5^{I}), 6.74 (d, 1 H, aromatic-5^{III}), 4.44 (d, 1 H, CH_2), 4.32 (dd, 1 H, CH'_2), ca. 1.96 (s, 6 H, CH_3,). − FAB-MS: calcd. for $[Ag_3(\mathbf{2})_2](PF_6)_2^+$: 1762.9, found: 1763.1; calcd. for $\{[Ag_3(\mathbf{2})_2](PF_6)\}^{2+}$: 1614.2, found: 1617.2; calcd. for $[Ag_3(\mathbf{2})_2]^{3+}$: 1469.2, found: 1471.2.

Titration of Ligand **1** *with Ag^I:* 2 mg of dimer **1** (5.3 μmol) was weighed into an NMR tube and dissolved in 0.5 ml of CD_2Cl_2. The solution was then titrated with a 0.125 M $AgPF_6$ solution. NMR spectra were recorded with 70 scans after addition of 7 μl (0.17 equiv.), 14 μl (0.33 equiv.), 19 μl (0.45 equiv.), 24 μl (0.57 equiv.), 31 μl (0.74 equiv.), 37 μl (0.88 equiv.), 42 μl (1 equiv.), 47 μl (1.12 equiv.), 52 μl (1.24 equiv.), 57 μl (1.36 equiv.) 63 μl (1.5 equiv.), 70 μl (1.67 equiv.), 80 μl (1.91 equiv.), 90 μl (2.15 equiv.), 100 μl (2.39 equiv.), 110 μl (2.63 equiv.) and 130 μl (3.11 equiv.) of the Ag^I solution. Equivalents refer to mols of binding site.

Titration of Ligand **2** *with Ag^I:* 4.8 mg of trimer **2** (8.4 μmol) was weighed into an NMR tube and dissolved in 0.5 ml CD_2Cl_2. A solution of AgTf in CD_3CN (78 mM) was prepared. NMR spectra (200 MHz) were recorded with 50 scans after addition of 30 μl (0.28 equiv.), 45 μl (0.42 equiv.), 60 μl (0.56 equiv.), 75 μl (0.7 equiv.), 100 μl (0.84 equiv.), 130 μl (1.12 equiv.), 150 μl (1.31 equiv.), 170 μl (1.50 equiv.), 185 μl (1.64 equiv.) and 205 μl (1.83 equiv.) of the Ag^I solution. Equivalents refer to mols of binding site.

Competition Experiment: 2 mg of dimer **1** (5.3 μmol) and 2 mg of trimer **2** (3.5 μmol) corresponding to 21.1 μmol binding sites were given into an NMR tube and dissolved in 0.75 ml of CD_2Cl_2. The solution was then titrated with a 0.125 M $AgPF_6$ solution. NMR spectra were recorded with 70 scans after addition of successive amounts of Ag^I solution from 7 μl (0.042 equiv.) to 207 μl (1.23 equiv.) in 7−10 μl aliquots. Equivalents refer to mols of binding site, so helicity should be complete after addition of 0.5 equiv.

UV Titration of Ligand **1** *with* Cu^{I}*:* A stock solution of 23.5 μM dimer **1** in dichloromethane was prepared. 1 ml of this solution containing 23.5 nmol of dimer was titrated with a 0.43 mM solution of $[Cu(CH_3CN)_4](PF_6)$ in dichloromethane/acetonitrile (1:1). UV spectra were recorded after addition of successive amounts of Cu^{I} solution from 10 μl (0.18 equiv.) to 260 μl (4.76 equiv.) in 10−15-μl aliquots. Equivalents refer to mols of binding site. Absorption values and spectra were automatically corrected for dilution by an internal ADL program of the Cary spectrophotometer.

UV Titration of Ligand **2** *with* Cu^{I}*:* A stock solution of 28.7 μM of trimer **2** in dichloromethane was prepared. 1 ml of this solution containing 28.7 nmol of the trimer was titrated with a 0.43 mM solution of $[Cu(CH_3CN)_4](PF_6)$ in dichloromethane/acetonitrile (1:1). UV spectra were recorded after addition successive amounts of Cu^{I} solution from 10 μl (0.15 equiv.) to 180 μl (2.69 equiv.) in 10-μl aliquots. Equivalents refer to mols of binding site. Absorption values and spectra were automatically corrected for dilution by an internal ADL program of the Cary spectrophotometer.

[1] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565−2569.
[2] E. C. Constable, *Tetrahedron* **1992**, *48*, 10013−10059; C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005.
[3] J.-M. Lehn, *Supramolcular Chemistry*, VCH, Weinheim, **1995**, chapter 9.
[4] J.-M. Lehn, A. Rigault, *Angew. Chem.* **1988**, *100*, 1121−1122; *Angew. Chem. Int. Ed. Engl* **1988**, *27*, 1059−1060.
[5] [5a] R. F. Carina, G. Bernardinelli, A. F. Williams, *Angew. Chem.* **1993**, *105*, 1483−1485; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1463−1465. − [5b] C. Piguet, J. C. G. Bünzli, G. Bernardinelli, G. Hopfgartner, A. F. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 8197−8206.
[6] R. Krämer, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem.* **1993**, *105*, 764−767; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 703−706.
[7] [7a] T. M. Garrett, U. Koert, J.-M. Lehn, A. Rigault, D. Meyer, J. Fischer, *J. Chem. Soc., Chem. Commun.* **1990**, 557−558. − [7b] U. Koert, M. M. Harding, J.-M. Lehn, *Nature* **1990**, *346*, 339−342.
[8] W. Zarges, J. Hall. J.-M. Lehn, C. Bolm, *Helv. Chim. Acta* **1991, 74**, 1843−1852.
[9] R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 5394−5398.
[10] C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani, A. F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 7440−7451.
[11] B. Hasenknopf, J.-M. Lehn, *Helv. Chim. Acta* **1996**, *79*, 1643−1650.
[12] [12a] A. Pfeil, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* **1992**, 838−840. − [12b] T. M. Garrett, U. Koert, J.-M. Lehn, *J. Phys. Org. Chem.* **1992**, *5*, 529−532.
[13] U. Koert, J.-M. Lehn, unpublished work, ULP Strasbourg, **1990**.
[14] J.-M. Lehn, R. Ziessel, *Helv. Chim. Acta* **1988**, *71*, 1511−1516.
[15] M.-T. Youinou, R. Ziessel, J.-M. Lehn, *Inorg. Chem.* **1991**, *30*, 2144−2148.
[16] [16a] Y. He, J.-M. Lehn, *Chem. J. Chinese Univ.* **1990**, *6*, 183−188. − [16b] D.-P. Funeriu, Y. He, H.-J. Biester, J.-M. Lehn, *Bull. Soc. Chim. Fr.* **1996**, *133*, 673−678.
[17] N. Blazevic, D. Kolbah, B. Belin, V. Sunjic, F. Kajfez, *Synthesis* **1979**, 161−176.
[18] B. Alpha, E. Anklam, R. Deschenaux, J.-M. Lehn, M. Pietraskiewicz, *Helv. Chim. Acta* **1988**, *71*, 1042−1052.
[19] G. R. Newkome, W. E. Puckett, G. E. Kiefer, V. K. Gupta, Y. Xia, M. Coreil, M. A. Hackney, *J. Org. Chem.* **1982**, *47*, 4116−4120.
[20] K. Nakamoto, *J. Phys. Chem.* **1960**, *64*, 1420−1425.
[21] E. Müller, C. Piguet, G. Bernardinelli, A. F. Williams, *Inorg. Chem.* **1988**, *27*, 849−855.
[22] A. Pfeil, J.-M. Lehn, unpublished work, ULP Strasbourg, **1991**.
[23] J. S. Lindsey, *New J. Chem.* **1991**, *15*, 133−180.
[24] [24a] G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90−92. − [24b] B.J. Hathaway, D. G. Holah, J. D. Postlethwaite, *J. Chem. Soc.* **1961**, 3215−3218.
[25] G. R. Newkome, D. C. Pantaleo, W. E. Puckett, P. L. Ziefle, W. A. Deutsch, *J. Inorg. Nucl. Chem.* **1981**, *43*, 1529−1531.
[26] T. Rode, E. Breitmeier, *Synthesis* **1987**, 574−576.
[27] J.-C. Rodriguez-Ubis, B. Alpha, D. Plancherel, J.-M. Lehn, *Helv. Chim. Acta* **1984**, *67*, 2264−2269.
[28] G. R. Newkome, V. K. Gupta, F. R. Fronzcek, *Inorg. Chem.* **1983**, *22*, 171−174.
[29] A. Marquis, J.-M. Lehn, work in progress.

[98028]