Synthesis of Dicopper [3]-Catenates and [3]-Catenands by Acetylenic Oxidative Coupling. Preparation and Study of Corresponding Homodimetallic [3]-Catenates (Ag^+, Zn^{2+}, Co^{2+}, and Ni^{2+})[†]

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Abstract: [3]-Catenates have been prepared in good yield by double acetylenic oxidative coupling from a terminal diyne threaded into a preformed ring. The central macrocyle is a 44-membered ring, whereas the peripheral subunits consist of 27- or 30-membered rings; the dicopper [3]-catenates are obtained in 68% or 58% yield, respectively. Besides these molecular systems containing three interlocked rings, a significant proportion of [4]-catenates was also isolated, the overall yield of interlocking cyclic products thus amounting to 80%. The corresponding [3]-catenands could be prepared by removal of the templating copper(I) centers by KCN. Remetalation of a [3]-catenand by various transition metals (Ag^+, Zn^{2+}, Co^{2+}, or Ni^{2+}) led to new symetrical dimetallic species. These complexes were fully characterized. A detailed electrochemical study showed some electrostatic interaction between the cationic complex subunits within the same molecule, provided the system was folded up so as to bring the two subcomplexes to a relative proximity. Some indication about the geometry of the molecule in solution could thus be obtained by electrochemical measurements.

Introduction

Catenands[1] combine the topological properties of catenanes[2,3] and other molecular systems having a nonplanar graph[4,5] with the complexing ability of 1,10-phenanthroline-type chelates.[6] [2]-Catenands consist of two coordinating interlocked rings, the prototype of which being formed by two 30-membered rings. The coordinating ability of this compound[7] and the spectro-, electro-, and photochemical properties of many of its corresponding complexes, the catenates, have been studied in detail[8] as well as some kinetic characteristics of these compounds.[9]

We have extended the 3D-template synthesis of interlocked rings to [3]-catenands by using the same basic reactions as for [2]-catenands.[10] Unfortunately, cyclization yields were very poor (2–6%), and workup procedures were tedious. [3]-Catenanes have previously been obtained by Schill et al.,[11] following a multistep-directed synthesis.

Recently, a high-yield synthesis of dicopper(I) [3]-catenates was developed,[12] by using an acetylenic oxidative coupling as a cyclization reaction. The strategy corresponds to a cyclodimerization, involving four reaction centers only (see Figure 1), in contrast to the previously reported synthesis which required eight centers to be linked.[10] We now describe the procedure in detail as well as its generalization. In addition, we report that copper(I) can be replaced in the [3]-catenates by various cationic species (H^+, Ag^+, Zn^{2+}, Co^{2+}, and Ni^{2+}), leading to new homodinuclear [3]-catenates whose properties are also described and compared to those of the corresponding [2]-catenates.

Results and Discussion

1. Synthesis of the Dicopper(I) [3]-Catenates $Cu_2{\cdot}7^{2+}$ and $Cu_2{\cdot}8^{2+}$. The principle of the cyclodimerization strategy is given in Figure 1. The acetylenic oxidative coupling turned out to be remarkably efficient in the synthesis of [3]-catenands following the strategy of Figure 1. The Glaser reaction (oxidative coupling of terminal acetylenes) has been used for many years in the construction of macrorings. By intramolecular coupling, macrocyclic diynes have been obtained, whereas tetraynes are produced by oxidative cyclodimerization of molecular threads bearing acetylenic functions at their ends.[13,14] Several rigid cyclophanes designed as molecular receptors have been made utilizing this oxidative coupling reaction,[15] including a cyclohexayne obtained in noticeably high yield by cyclodimerization of a triyne.[16] Glaser reaction turned out to be also remarkably efficient for building multirings systems.

The precursors used, the reaction scheme, and the products obtained are represented in Figure 2. The open chain diyne **2** was prepared by reacting the diphenol **1** with propargyl bromide in dimethylformamide (DMF) at 65 °C, under argon, in the presence of Cs_2CO_3 in large excess. After chromatographic separation over silica gel, **2** was obtained as a white solid (mp 273–274 °C) in 80% yield. In the presence of stoichiometric amounts of the coordinating macrocycle **3** or **4** (27- or 30-membered rings, respectively, prepared as earlier described[17]) and $Cu(CH_3CN)_4^+{\cdot}BF_4^-$, the tripartite compound $\mathbf{5}^+$ or $\mathbf{6}^+$ is formed (CH_2Cl_2–CH_3CN 2:1 at room temperature for a few minutes; reaction monitored by thin-layer chromatography (TLC) leading to a product of sufficient purity without further workup than solvent evaporation). These complexes are obtained in nearly 100% yield

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[†] This paper is dedicated to the memory of Madjid Sedrati.

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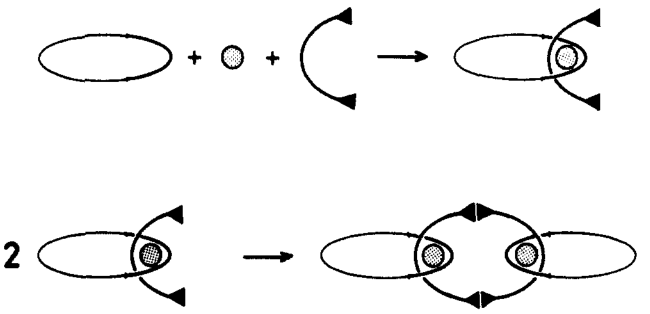

Figure 1. Synthesis of a [3]-catenate by cyclodimerization of a difunctional precursor. The coordinating fragments are shown as thick lines. The circles represent the templating transition metals.

as deep red solids. It is noteworthy that the formation reaction of 5^+ or 6^+ is quantitative if the stoichiometry of the **2**, **3**, or **4** and $Cu(CH_3CN)_4^+$ mixture is exactly 1:1:1. Two macroring ligands (**3** or **4**) cannot form bis-chelate complexes with copper(I), because the polyoxyethylene fragment prevents the 2,9-diphenylphenanthroline (dpp) subunits from getting entwined around a metal center. Thus, if the three-component complex (5^+ or 6^+) was not the sole product of the reaction, this would imply that a given proportion of the entwined complex $Cu(2)_2^+$ would also be formed, besides the same amount of free macrocyclic ligand (**3** or **4**) and the little stable macrocyclic complex $Cu\cdot 3^+$ or $Cu\cdot 4^+$. This situation is thermodynamically strongly disfavored since bis-chelate complexes of copper(I) are extremely stable with dpp-type ligands[7] (like in 5^+ or 6^+) or 2,9-dimethyl-1,10-phenanthroline.[18] In other words, the driving force for the formation of 5^+ or 6^+ is coordination to copper, the high stability of bis-chelate copper(I) complexes ensuring complete formation of this tripartite species.

The oxidative coupling reaction leading to the [3]-catenate $Cu_2\cdot 7^{2+}$ or $Cu_2\cdot 8^{2+}$ from 5^+ or 6^+, respectively, was carried out at room temperature in DMF, with copious amounts of CuCl and $CuCl_2$ (140 and 24 equiv, respectively, with respect to 5^+ or 6^+). We found the presence of air to be crucial, almost no detectable cyclization product being isolated when the reaction was performed under anaerobic conditions. Interestingly, the yields were found to be better in relatively concentrated solutions. Typically, a 7×10^{-3} M solution of 6^+ in DMF (containing 1 M CuCl and 0.2 $CuCl_2$) was stirred magnetically in air for 3 days. Such a procedure makes the preparation of $Cu_2\cdot 7^{2+}$ or $Cu_2\cdot 8^{2+}$ convenient, as compared to classical high dilution conditions requiring large volumes of solvent and fast and efficient stirring.[10,19] After column chromatography (silica, CH_2Cl_2, and small amounts of CH_3OH as eluent), the [3]-catenate $Cu_2\cdot 7^{2+}$ or $Cu_2\cdot 8^{2+}$ is isolated (BF_4^- salt) in 68% or 58% yield, respectively. $Cu_2\cdot 7^{2+}\cdot 2BF_4^-$ and $Cu_2\cdot 8^{2+}\cdot 2BF_4^-$ are highly crystalline deep red solids (mp > 300 °C, dec). The dicopper complex $Cu_2\cdot 7^{2+}$ consists of two peripheral 27-membered rings separately interlocked to a bis-diacetylenic 44-membered central cycle (27:44:27). $Cu_2\cdot 8^{2+}$ is formed of two 30-membered rings and the same central 44-membered ring as that of $Cu_2\cdot 7^{2+}$ (30:44:30).

Higher catenates were also isolated in significant proportion. Besides $Cu_2\cdot 8^{2+}$, the [4]-catenate corresponding to the cyclotrimerization product of 6^+ and containing three copper(I) centers and four interlocked rings (a central hexayne 66-membered ring and three peripheral cycles composed of **4**) was also obtained in 20% yield. Similarly, a [4]-catenate is obtained in 14% yield by cyclotrimerization of the precursor 5^+. Here again, the large central ring is a 66-membered cyclohexayne; the latter is now interlocked with three 27-membered macrocycles **3**.

At the present stage, these [4]-catenates are not sufficiently well characterized, and thus we will not discuss them anymore in the present article.

$Cu_2\cdot 7^{2+}$ and $Cu_2\cdot 8^{2+}$ have been fully characterized. Elemental analysis, UV-visible spectra, and ^{1}H-NMR data are given in the Experimental Section. The solid-state structure of $Cu_2\cdot 8^{2+}\cdot 2BF_4^-$ has been solved by X-ray crystallography,[20] whereas a detailed ^{1}H-NMR study gave clear evidence that the molecular shape of $Cu_2\cdot 8^{2+}$ is approximately the same in the CH_2Cl_2 solution and in the crystal.[20] Indeed, the molecule does not at all occupy an extended geometry as the drawing ($Cu_2\cdot 7^{2+}$ or $Cu_2\cdot 8^{2+}$) of Figure 2 would suggest, but rather it is completely curled up so as to allow close contact between various parts of the two copper(I) complex subunits. The analogy between the ^{1}H-NMR spectra of $Cu_2\cdot 7^{2+}$ and $Cu_2\cdot 8^{2+}$ in CD_2Cl_2 supports the idea that also for the smaller [3]-catenate $Cu_2\cdot 7^{2+}$, the molecular shape is governed by a complete folding up of the large central ring in order to permit interactions between both copper(I) subcomplexes.

Table I. Preparation of Various [3]-Catenates $M_2\cdot 8^{n+}$

starting salt	[3]-catenate obtained	preparative yield (%)
$AgBF_4$	$Ag_2\cdot 8^{2+}$	99
$Zn(ClO_4)_2\cdot 6H_2O$	$Zn_2\cdot 8^{4+}$	78
$Co(BF_4)_2\cdot 6H_2O$	$Co_2\cdot 8^{4+}$	65
$Ni(BF_4)_2\cdot 6H_2O$	$Ni_2\cdot 8^{4+}$	49

2. Preparation and Mass Spectrometry Study of the [3]-Catenands 7 and 8. As for other copper(I) catenates,[21] demetalation of $Cu_2\cdot 7^{2+}$ and $Cu_2\cdot 8^{2+}$ was performed with excess KCN in CH_2Cl_2–H_2O at room temperature. The [3]-catenands **7** and **8** were obtained in 76% and 75% yield, respectively. These compounds are white solids (mp 197–199 °C for **7** and 183–184 °C for **8**). They are almost insoluble in classical organic solvents. For instance, the ^{1}H-NMR spectrum of **8** had to be measured in CD_3SOCD_3 at 100 °C. By analogy with the (30:30) [2]-catenand previously studied,[21] the ^{1}H-NMR spectrum of **8** clearly shows the disentangling of the dpp fragments.

Compounds **7** and **8** were characterized by C, H, N elemental analysis, ^{1}H-NMR, and mass spectrometry. The latter method turned out to be especially interesting for these interlocked structures. The mass spectrum of **8** is shown in Figure 3.

The general pattern of the spectrum is very characteristic of catenanes, as previously observed by Schill, Vetter, and coworkers.[22] The stepwise cutting up and release of each ring from the system is clearly observed by the presence of molecular peaks corresponding to (30:44:30), (30:44), and (44). This behavior is analogous to other previously prepared [3]-catenands.[10]

3. Preparation and Study of Various Symmetrical Dimetallic [3]-Catenates (Cu^+, Ag^+, Zn^{2+}, Co^{2+}, Ni^{2+}). The Cu···Cu distance found in the X-ray structure of $Cu_2\cdot 8^{2+}$ is 8.5 Å.[20] This is probably too long to allow strong electronic interactions between two metal centers. However, some kind of interaction between paramagnetic centers can be envisaged since recent studies have shown that two copper(II) centers can communicate at distances up to 11.2 Å.[23] The space between the metal centers of dinuclear complexes of **8** is filled up with stacking aromatic nuclei in the folded conformation, which could result in interesting effects. More generally, we were curious to compare the electrochemical and photophysical parameters of dimetallic [3]-catenates to the corresponding [2]-catenates.[8] We wished to estimate the effect of one complex subunit on the properties of the other. This prompted us to prepare and study several dinuclear species.

The various [3]-catenates prepared were obtained very simply by mixing **8**, suspended in CH_2Cl_2, and a metal salt usually taken in excess. After stirring at room temperature and workup, the [3]-catenates were isolated in relatively good yields as crystalline solids. The formation reaction could be monitored by TLC (silica,

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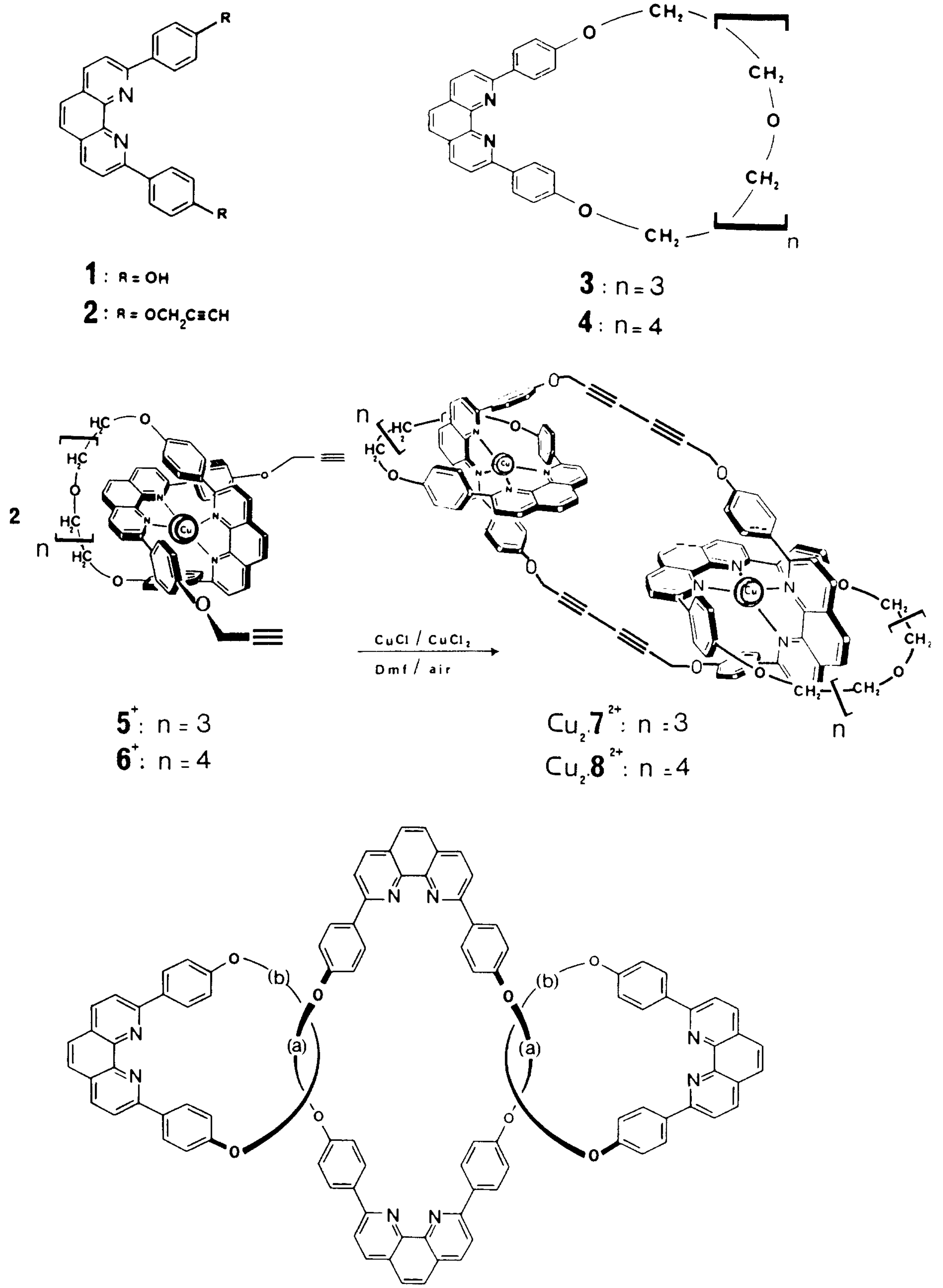


(a) : $-CH_2-C\equiv C-C\equiv C-CH_2-$

(b) : $-CH_2CH_2(O-CH_2CH_2)_n$ **7**: n = 3 ; **8**: n = 4

Figure 2.

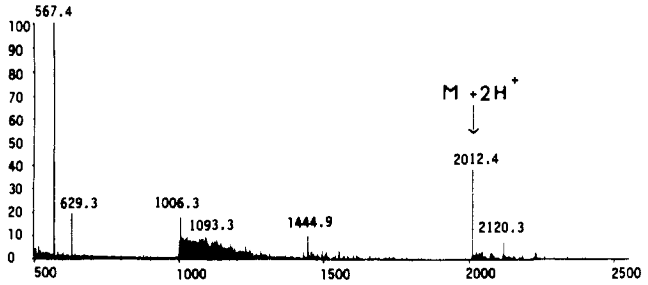
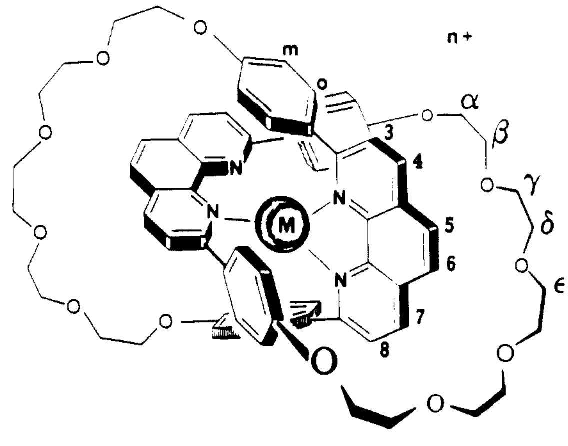


Figure 3. Mass spectrum of the [3]-catenand **8** (FAB).

Chart I



M.9^{n+}

M = Cu^+, Cu·$\mathbf{9}^+$
M = Ag^+, Ag·$\mathbf{9}^+$
M = Zn^{2+}, Zn·$\mathbf{9}^{2+}$
M = Co^{2+}, Co·$\mathbf{9}^{2+}$
M = Ni^{2+}, Ni·$\mathbf{9}^{2+}$

CH_2Cl_2–CH_3OH as eluent). The [3]-catenates synthesized are listed in Table I with the corresponding preparation yield.

The cadmium(II) catenate Cd_2·$\mathbf{8}^{4+}$ could not be obtained following the procedure applied to the other catenates of **8**. Rather, a diprotonated species H_2·$\mathbf{8}^{2+}$ was obtained as a lemon yellow solid. This compound is reminiscent of the monoprotonated species of the [2]-catenand[24] (30:30). In particular, the ^{1}H-NMR spectrum shows unambiguously that H_2·$\mathbf{8}^{2+}$ is disposed in an entwined arrangement, each proton being located in a N_4 coordination site, very similar to the metallic [3]-catenates of **8**.

The Ag^+, H^+, Zn^{2+}, Co^{2+}, and Ni^{2+} [3]-catenates of **8** have C, H, N elemental analysis and fast atom bombardment (FAB) mass spectra in agreement with their proposed structures. As for other catenates[1,17,21] ^{1}H NMR turned out to be highly informative with respect to the general molecular shape of the systems: H_2·$\mathbf{8}^{2+}$, Ag_2·$\mathbf{8}^{2+}$, and Zn_2·$\mathbf{8}^{4+}$ have spectra characteristic of the "entwined topography", with dpp subunits fitting in together. As a consequence of this particular shape, with some particular protons like H_o, H_m, and CH_2 (see Figure 4) becoming located above and below the 1,10-phenanthroline nuclei, the corresponding resonance signals move to high field as compared to the free ligand spectrum. A typical example is the silver(I) complex Ag_2·$\mathbf{8}^{2+}$ whose ^{1}H-NMR spectrum is given in Figure 4. For this compound, the H_o, H_m, and CH_2 signals are shifted upfield by 1.04, 1.13, 0.87, 0.98, and 0.30 ppm, respectively, upon complexation.

The electrochemical properties of the dimetallic [3]-catenates prepared from Cu_2·$\mathbf{7}^{2+}$ and Cu_2·$\mathbf{8}^{2+}$ have been studied and compared to those of the corresponding (30:30) [2]-catenates whose preparation from **9** and electrochemical parameters have recently been reported.[8] The structure of the [2]-catenates is depicted in Chart I. The electrochemical data are collected in Table II.

Table II. Electrochemical Properties of Homodimetallic [3]-Catenates and Comparison to the Corresponding Monometallic [2]-Catenates[a]

	oxidation	reduction		
complex	1st wave	1st wave	2nd wave	$\Delta E_{[3]-[2]}$
Cu_2·$\mathbf{8}^{2+}$	+0.670	-1.610_{ir}	-1.830_{ir}	+0.00
Cu·$\mathbf{9}^{+\,b}$	+0.565	-1.610^g	-1.815^g	
Ag_2·$\mathbf{8}^{2+}$	*c*	-0.540^d		+0.16
Ag·$\mathbf{9}^{+\,b}$	*c*	-0.700^e		
Zn_2·$\mathbf{8}^{4+}$	*c*	-0.970_{ir}	-1.340_{ir}	−0.01
Zn·$\mathbf{9}^{2+\,b}$	*c*	$-0.960_{qr}^{(f)}$	$-1.260_{qr}^{(f)}$	
Co_2·$\mathbf{8}^{4+}$	*c*	−0.450	−1.243	+0.15
Co·$\mathbf{9}^{2+\,b}$	*c*	−0.600	−1.315	
Ni_2·$\mathbf{8}^{4+}$	*c*	−0.080	−1.295	+0.10
Ni·$\mathbf{9}^{2+}$	*c*	−0.180	−1.325	

[a] Redox potential (V) measured in CH_3CN vs the saturated calomel electrode (SCE), determined by cyclic voltammetry at the platinum electrode; supporting electrolyte, 0.1 M $(nC_4H_9)_4N^+$·BF_4^-; room temperature under argon; scan rate, 100 mV s^{-1}; the systems are reversible except in a few cases indicated by qr (quasi-reversible) and ir (irreversible). [b] Taken from ref 8. [c] No oxidation wave is detected before irreversible oxidation of the ligand ($E > 1.5$ V). [d] Polarography measurement at the dropping mercury electrode (DME) in CH_2Cl_2. [e] Polarography measurement at the dropping mercury electrode (DME) in CH_3CN. [f] In CH_2Cl_2. [g] In DMF; Hg electrode. [h] $\Delta E_{[3]-[2]}$ = difference between the first reduction wave respectively observed for a given [3]-catenate and the analogous [2]-catenate.

Most of the [3]-catenates studied show highly reversible electroreductive processes. A typical example is that of Co_2·$\mathbf{8}^{4+}$ for which the cyclic voltammogram is represented in Figure 5.

An interesting effect is found by comparing the first reduction potentials of the mono- and dimetallic complexes. The differences between those redox potentials, $\Delta E_{[3]-[2]}$, are listed in Table II. They reflect the greater tendency of the [3]-catenates to be reduced as compared to their monometallic analogues. Clearly, most of the [3]-catenates are more easily reduced than their corresponding [2]-catenate by 0.1–0.2 V, although the electronic properties (σ and π electron-donating and -accepting character) of the individual coordinating species are identical for both systems. A possible explanation is that in [3]-catenates the reduced species is slightly stabilized by electrostatic interaction with the positively charged second subcomplex. Whether this stabilizing charge effect occurs only from center-to-center or via the voluminous π system of the ligands is uncertain as yet, although the second contribution seems to be relatively likely to be important in view of the large metal-to-metal distance (8.5 Å) found in the structure of Cu_2·$\mathbf{8}^{2+}$ [20] and assuming that the metals cannot get much closer in other complexes due to steric repulsion within the organic skeleton of the ligand.

Interestingly, Zn_2·$\mathbf{8}^{4+}$ and Zn·$\mathbf{9}^{2+}$ [8] are reduced at almost exactly the same potential. This may be an indication that the [3]-catenate is less curled up in this case, possibly because of too strong an electrostatic repulsion between the two hard and dicationic zinc(II) centers. ^{1}H-NMR data corroborate this hypothetical more extended conformation of Zn_2·$\mathbf{8}^{4+}$. The chemical shift of the $H_{3,8}$ signals can be considered as a good probe for the curling up of the molecule.[20] From the values collected in Table I, it is clear that Cu·$\mathbf{9}^+$ [8] and Cu_2·$\mathbf{8}^{2+}$ have noticably different $H_{3,8}$ chemical shifts ($\Delta\delta_{H_{3,8}}$ = +0.19 and +0.45 ppm) which accounts for the folded conformation of the dinuclear [3]-catenate. By contrast, the $H_{3,8}$ signals of Zn·$\mathbf{9}^{2+}$ and Zn_2·$\mathbf{8}^{4+}$ are found at more similar fields ($\Delta\delta_{H_{3,8}}$ = +0.11 and +0.24 ppm), in agreement with less curling up for Zn_2·$\mathbf{8}^{4+}$ as compared to the dicopper(I) complex.

Conclusion

The template synthesis of bis-diacetylenic [3]-catenates (and even their upper homologues) has been achieved in surprisingly

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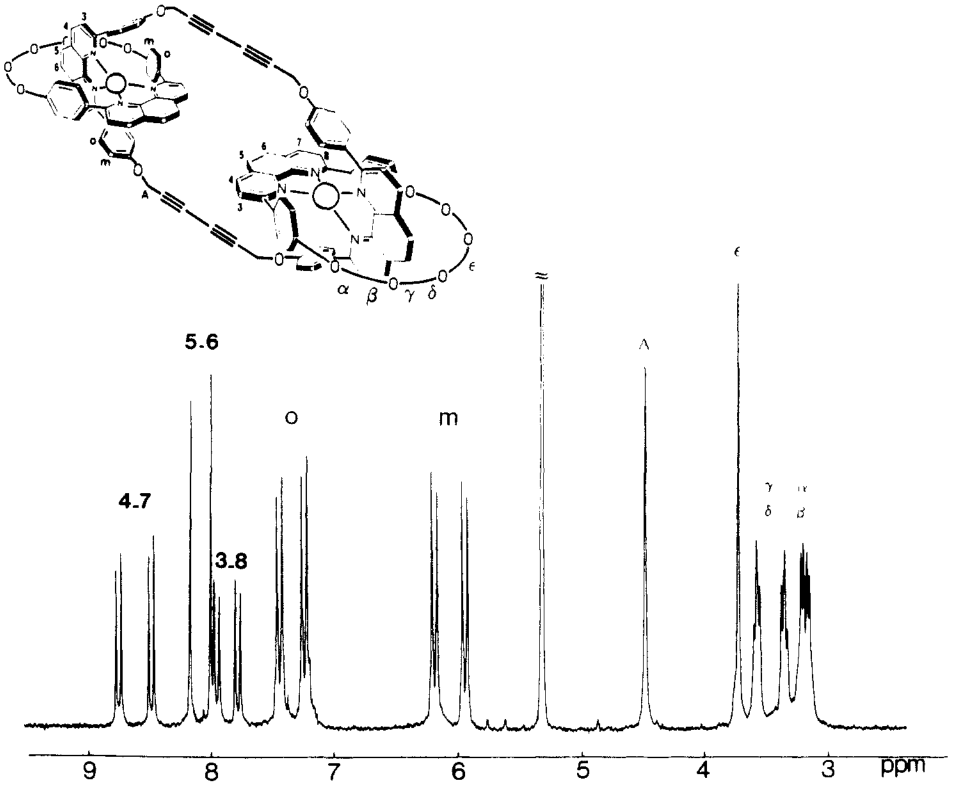

Figure 4. 200-MHz ^{1}H-NMR spectra of $Ag_2 \cdot 8^{2+}$ in CD_2Cl_2. The circles represent the silver(I) cations.

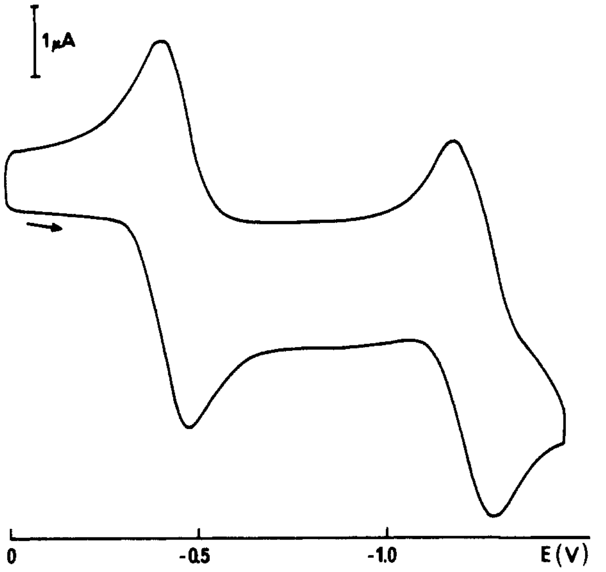

Figure 5. Cyclic voltammogram of $Co_2 \cdot 8^{4+}$ (4.2×10^{-4} mol·L^{-1}) in $CH_3CN-(nC_4H_9)_4N^+ \cdot BF_4^-$ 0.1 mol·L^{-1} (Pt, scan rate 100 mV × s^{-1}, E vs SCE).

high yield, by using the oxidative coupling reaction of terminal acetylenes. This procedure allows gram-scale preparation of a (30:44:30) system which could easily be demetalated, affording a novel coordinating system ([3]-catenand). By recomplexation with various transition metals, a series of symmetrical dimetallic catenates was obtained. Electrochemical measurements shed light onto the molecular shape of the system in solution. When the molecule was in an extending conformation provided a large metal-to-metal separation, no electrostatic interaction was observed. In other cases, the folding up of the system could be shown by electrostatic interactions detected by cyclic voltamperometric measurements.

Experimental Section

General Methods. Acetonitrile was dried and purified by distillation (normal pressure) over CaH_2. $Cu(CH_3CN)_4 \cdot BF_4$ was prepared by the literature method.[25] Alternatively, $Cu(CH_3CN)_4 \cdot BF_4$ was prepared by reduction of $Cu(BF_4)_2$ by copper powder (excess) in CH_3CN under argon at room temperature, the mixture being stirred until complete bleaching of the solution was effected. Anhydrous copper(I) and copper(II) chlorides were prepared according to literature.[26,27] Dimethylformamide (DMF) was first dried over activated alumina (grade I), filtered, and afterwards distilled under argon at reduced pressure (bp 40 °C/10 mmHg). The distillate was stored over a type 4A molecular sieve. All other chemicals were of the best commercially available grade and were used without further purification. ^{1}H-NMR spectra were recorded with a Bruker WP 200 SY spectrometer. All compounds based on diphenylphenanthroline show a highly characteristic pattern: a singlet for H_5 and H_6, an AB pattern for H_3 or H_8 and H_4 or H_7 (coupling constant $J \simeq 8.5$ Hz), and an AA'XX' system ($J \simeq 8.7$ Hz) for H_o and H_m. H' designates the protons belonging to large central macrocycle m-44. H designates the protons belonging to the small lateral rings m-27 or m-30.

Electronic spectra were performed with Varian Cary 118 or with Kontron Unikon 80 spectrometers.

Emission spectra were obtained with a Shimadzu RF 450 spectrometer. The solutions were degassed by three freeze-thaw-pump cycles.

Mass spectra were recorded on a Thomson THN 208 (chemical ionization) or on a ZAB-HF (FAB).

Melting points were measured with a Reichert microscope or with a Büchi SMP-20 melting point apparatus.

Preparation of the Diyne Phenanthroline 2. A degassed solution of **1** (0.982 g, 2.7 mmol) in DMF (30 mL) was added dropwise within 1 h under efficient stirring to an argon-flushed suspension of Cs_2CO_3 (3 g, 9.2 mmol) in 250 mL of DMF kept at 55–60 °C. After this addition the resulting suspension had a brown-red color; stirring and heating was continued for 1 h after which slow addition of propargyl bromide (0.702 g, 5.9 mmol) in degassed DMF (20 mL) was started. During this addition (2 h) the temperature was kept between 55 and 60 °C, and the suspension turned progressively yellow. Stirring and heating was further continued for 24 h. DMF was then evaporated, and the dry residue was taken up in $H_2O-CH_2Cl_2$. The aqueous layer was extracted with three 100-mL portions of CH_2Cl_2; combined organic layers were dried over $MgSO_4$, filtrated, and evaporated to dryness: crude **2** was thus obtained

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Table III. Electronic Properties of Homodimetallic [3]-Catenates

complex	absorption[a] λ_{max}(nm) [10^{-3} ϵ, mol^{-1} L cm^{-1}]	emission[a] λ_{ex}[b] (nm)	emission[a] λ_{em} (nm)
$Cu_2\cdot 7^{2+}$	241.5 [146.4], 277.5 [113.6], 316.0 [92.3], 457.5 [6.0]		
$Cu_2\cdot 8^{2+}$	249.0 [143.0], 276.5 [128.7], 326.0 [93.5], 441.0 [4.4]	444.0	690.0
$Ag_2\cdot 8^{2+}$	240.0 [146.8], 280.0 [116.4], 316.0 [96.4]	324.0	400.0
$Zn_2\cdot 8^{4+}$	232.5 [98.5], 251.0 [98.5], 275.0 [84.5] sh, 290.5 [77.6], 310.0 [73.7], 341.0 [61.7]	355.0	460.0
$Co_2\cdot 8^{4+}$	231.5 [126.8], 253.0 [119.5], 296.0 [89.5], 310.0 [91.2]	342.0	405.0
$Ni_2\cdot 8^{4+}$	230.5 [108.4], 215.5 [98.0], 292.0 [71.6] sh, 319.5 [72.3]		
$H_2\cdot 8^{2+}$	238.0 [110.9], 278.0 [105.2], 342.0 [58.0]	350.0	396.0

[a] In CH_2Cl_2. [b] This wavelength was chosen as the excitation spectrum maximum.

quantitatively (1.188 g) as a yellow solid. Column chromatography on silica gel (eluent CH_2Cl_2/hexane, 50:50) gave 0.926 g of pure compound **2** (78% yield, pure CH_2Cl_2).

Diyne Phenanthroline 2: pale yellow needles (mp 273–274 °C); ^1H-NMR (CD_2Cl_2) 8.44 (d, 4 H, H_o), 8.31 (d, 2 H, H_4 or H_7), 8.12 (d, 2 H, H_3 or H_8), 7.79 (s, 2 H, H_5 and H_6), 7.20 (d, 4 H, H_m), 4.83 (d, $J \simeq 2.40$ Hz, 4 H, $CH_2{-}C{\equiv}C$), 2.64 (t, $J \simeq 2.40$ Hz, 2 H, $C{\equiv}CH$). Anal. Calcd for $C_{30}H_{20}N_2O_2{\cdot}1H_2O$: C, 78.58; H, 4.83; N, 6.11. Found: C, 78.85; H, 4.46; N, 6.09.

Macrocyles 3 and 4 (See Refs 28 and 17). Precursor 5^+. By the double-ended needle transfer technique, 330 mg (1.05 mmol) of $Cu(CH_3CN)_4{\cdot}BF_4$ in degassed acetonitrile (30 mL) were added under argon and at room temperature to a stirred degassed solution of **3** (522 mg, 1 mmol) in CH_2Cl_2 (30 mL). Instantaneous appearance of a deep orange coloration in the solution was related to the formation of $Cu3^+$. After 0.5 h stirring at room temperature, a solution of **2** (440 mg, 1 mmol) in CH_2Cl_2 (50 mL) was added to the complex $Cu3^+$. The solution turned dark red immediately. After the solution was stirred for 1 h under argon at room temperature, the solvents were evaporated to dryness: dark red needles of crude 5^+ were obtained in quantitative yield (1235 mg, 1 mmol). Filtration over silica gel (eluent CH_2Cl_2) gave 925 mg of pure precursor 5^+ (83% yield, eluent CH_2Cl_2 containing 0.5 to 1% MeOH): 5^+, dark red solid was only characterized by ^1H NMR (CD_2Cl_2) 8.83 (d, 2 H, H'_4 or H'_7), 8.52 (d, 2 H, H_4 or H_7), 8.27 (s, 2 H, H'_5 and H'_6), 8.07 (s, 2 H, H_5 and H_6), 7.94 (d, 2 H, H'_3 or H'_8), 7.88 (d, 2 H, H_3 or H_8), 7.43 (d, 4 H, H'_o), 6.87 (d, 4 H, H_o), 6.15 (d, 4 H, H'_m), 5.78 (d, 4 H, H_m), 4.43 (d, $J \simeq 2.40$ Hz, 4 H, $CH_2{-}C{\equiv}C$), 3.90–3.81 (m, 8 H, $H_{\gamma,\delta}$), 3.52 (t, $J \simeq 5.30$ Hz, 4 H, H_β), 3.14 (t, $J \simeq 5.30$ Hz, 4 H, H_α), 2.56 (t, $J \simeq 2.40$ Hz, 2 H, $C{\equiv}CH$).

Precursor 6^+. By a procedure similar to the one described for 5^+, 6^+ was prepared by using the following: 453 mg (0.8 mmol) of **4** in 30 mL of CH_2Cl_2, 265 mg (0.84 mmol) of $Cu(CH_3CN)_4{\cdot}BF_4$ in 40 mL of CH_3CN, 352 mg (0.8 mmol) of **2** in 50 mL of CH_2Cl_2. After the solvents were evaporated, crude 6^+ was obtained as a dark red solid in quantitative yield (920 mg $\simeq$ 0.8 mmol). Filtration over silica gel (eluent CH_2Cl_2) yielded pure precursor 6^+ (833 mg, 90% yield). 6^+, dark red solid was only characterized by ^1H NMR (CD_2Cl_2) 8.64 (d, 2 H, H'_4 or H'_7), 8.47 (d, 2 H, H_4 or H_7) 8.24 (s, 2 H, H'_5 and H'_6), 8.02 (s, 2 H, H_5 and H_6), 7.88 (d, 2 H, H'_3 or H'_8), 7.84 (d, 2 H, H_3 or H_8), 7.50 (d, 4 H, H'_o), 7.28 (d, 4 H, H_o), 6.15 (d, 4 H, H'_m), 5.99 (d, 4 H, H_m), 4.37 (br s, 4 H, $CH_2{-}C{\equiv}C$), 3.83 (s, 4 H, H_ϵ), 3.73–3.49 (m, 16 H, $H_{\alpha,\beta,\gamma,\delta}$), 2.61 (br s, 2 H, $C{\equiv}CH$).

[3]-Catenate $Cu_2\cdot 7^{2+}$. Under highly anhydrous conditions 445 mg (0.4 mmol) of precursor 5^+, 5.346 g (54 mmol) of anhydrous CuCl, and 1.210 g (9 mmol) of anhydrous $CuCl_2$ were suspended in 60 mL of dry DMF in a simple one-necked, round-bottomed flask. The latter was stoppered with a drying tube filled with silica gel so that the mixture was protected against moisture but in contact with air. The dark brown-red suspension was magnetically stirred at room temperature during 3 days after which the DMF was evaporated to dryness. The almost black solid residue was taken up in 200 mL of CH_2Cl_2 and 200 mL of 5% HCl/H_2O solution. After decantation, the aqueous layer was extracted five times with 50-mL portions of CH_2Cl_2. The combined organic layers were washed twice with 100-mL portions of 5% HCl solution and once with pure H_2O. This wet CH_2Cl_2 phase was thereafter treated (overnight, magnetic stirring) with a large excess of $NaBF_4$ dissolved in a minimum of water. By means of this exchange reaction, we obtained $Cu_2\cdot 7^{2+}$, originally formed as chloride and tetrafluoroborate, exclusively as its BF_4^- salt. The resulting organic layer, washed twice with water, was dried over $MgSO_4$ and evaporated to dryness to yield 442 mg of crude dark red $Cu_2\cdot 7^{2+}$. Column chromatography on silica gel (eluent CH_2Cl_2/hexane, 50:50) gave 300 mg of pure $Cu_2\cdot 7^{2+}$ (68% yield, CH_2Cl_2 containing 0.5–2% MeOH) and 62 mg of [4]-catenate (yield 14%, CH_2Cl_2 containing 2–8% MeOH).

$Cu_2\cdot 7^{2+}$: dark red needles (mp >315 °C) ^1H NMR (see Table IV); absorption (see Table III); MS, M/2 calculated 1024.63, found 1024.41. Anal. Calcd for $C_{124}H_{96}N_8O_{14}Cu_2B_2F_8$: C, 67.00; H, 4.35; N, 5.04. Found: C, 66.97; H, 4.32; N, 5.04.

Demetalation of $Cu_2\cdot 7^{2+}$ To Afford 7. KCN (450 mg, 6.9 mmol) dissolved in water (10 mL) was added to $Cu_2\cdot 7^{2+}$ (43 mg, 0.019 mmol) in CH_2Cl_2 (10 mL) at room temperature. The characteristic dark red color of the magnetically stirred solution disappeared progressively, whereas free ligand **7**, insoluble in CH_2Cl_2, precipitated as a white solid. After 5 h, decoloration was complete. Solid **7** was then filtered over paper, washed carefully with water, and dried in air to yield 28 mg (76%) of colorless compound.

7: colorless solid (mp 244–245 °C) ^1H NMR (see Table IV); MS, calculated 1922.17, found 1922.70. Anal. Calcd for $C_{124}H_{96}N_8O_{14}$: C, 74.77; H, 4.88; N, 5.58. Found: C, 74.76; H, 4.95; N, 5.53.

[3]-Catenate $Cu_2\cdot 8^{2+}$. By a procedure similar to that described for $Cu_2\cdot 7^{2+}$, $Cu_2\cdot 8^{2+}$ was prepared with 298 mg (0.258 mmol) of precursor 6^+, 3500 mg (35.3 mmol) of CuCl, and 830 mg (6.2 mmol) of $CuCl_2$ in 40 mL of dry DMF. After stirring for 3 days at room temperature, workup gave crude $Cu_2\cdot 8^{2+}$ in quantitative yield (295 mg). Column chromatography on silica gel (eluent CH_2Cl_2/hexane, 50:50) gave 172 mg of pure $Cu_2\cdot 8^{2+}$ (58% yield, CH_2Cl_2 containing 3–4% MeOH) and 60 mg of [4]-catenate (yield 20%, CH_2Cl_2 containing 4–10% MeOH).

$Cu_2\cdot 8^{2+}$: dark red needles (mp >315 °C); ^1H NMR (see Table IV); absorption (see Table III); MS, M/2 calculated 1068.68, found 1068.55. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Cu_2B_2F_8$: C, 66.52; H, 4.54; N, 4.85. Found: C, 66.58; H, 4.57; N, 4.69.

Demetalation of $Cu_2\cdot 8^{2+}$ To Afford 8. Demetalation of $Cu_2\cdot 8^{2+}$ was achieved as for $Cu_2\cdot 7^{2+}$ with 64 mg (0.028 mmol) of $Cu_2\cdot 8^{2+}$ in 20 mL of CH_2Cl_2 and 500 mg (7.7 mmol) of KCN in 20 mL of water. After drying in air, 42 mg (75% yield) of **8** were obtained as a colorless solid.

8: colorless solid (mp 183–184 °C); ^1H NMR (see Table IV); MS, ($M + 2H^+$) calculated 2012.16, found 2012.4. Anal. Calcd for $C_{128}H_{104}N_8O_{16}$: C, 76.47; H, 5.21; N, 5.57. Found: C, 76.36; H, 5.15; N, 5.57.

Table IV. ^1H-NMR Spectra of **7**, **8**, **9**, and Their Complexes

compd	$H'_{4,7}$ $H_{4,7}$	$H'_{5,6}$ $H_{5,6}$	$H'_{3,8}$ $H_{3,8}$	$\Delta\delta$	H'_o H_o	H'_m H_m	$H'_{CH_2-C\equiv C}$	$H_{\alpha,\beta,\gamma,\delta,\epsilon}$
$Cu_2\cdot 7^{2+}$[a]	8.74	8.20	7.79		7.16	6.01	4.62	
	8.62	8.18	7.68		6.65	5.48		3.85–3.81 (m, $H_{\gamma,\delta}$), 3.50 (t, H_β), 2.96 (t, H_α)
8[c]	8.43 < m < 8.25	7.91	8.43 < m < 8.25		8.58	7.19	5.11	
		7.81			8.45	7.06		4.16 (t, H_α), 3.72–3.39 (m, $H_{\beta,\gamma,\delta,\epsilon}$)
$Cu_2\cdot 8^{2+}$[b]	8.47	8.16	7.67	+0.19	7.02	5.85	4.54	
	8.43	8.07	7.41	+0.45	6.77	5.40		3.77 (s, H_ϵ), 3.68–3.55 (m, $H_{\gamma,\delta}$), 3.32 (t, H_β), 3.05 (t, H_α)
$Cu\cdot 9^{+}$[b]	8.63	8.26	7.86		7.38	6.00		3.7. (s, H_ϵ), 3.67–3.55, –3.41 (m, $H_{\alpha,\beta,\gamma,\delta}$)
$Ag\cdot 8^{2+}$[a]	8.72	8.14	7.93		7.42	6.19	4.49	
	8.46	7.98	7.76		7.22	5.94		3.75 (s, H_ϵ), 3.60–3.38 (m, $H_{\gamma,\delta}$), 3.21 (m, $H_{\alpha,\beta}$)
$Zn_2\cdot 8^{4+}$[b]	8.93	8.43	8.00	+0.11	6.97	6.15	4.64	
	8.89	8.42	7.87	+0.24	6.85	5.85		3.83 (s, $H\epsilon$), 3.79–3.66 (m, $H_{\gamma,\delta}$), 3.51 (t, H_β), 3.31 (t, H_α)
$Zn\cdot 9^{2+}$[b]	8.97	8.55	8.11		7.37	6.22		3.82 (s, H_ϵ), 3.76–3.64 (m, $H_{\beta,\gamma,\delta}$), 3.50 (br s, H_α)
$H_2\cdot 8^{2+}$[b]	8.33	7.83	7.65		7.21	6.38	4.95	
	7.86	7.38	7.31		6.97	6.15		3.79 (t, H_α), 3.89–3.82 (m, $H_{\beta,\gamma,\delta,\epsilon}$)

[a] δ (ppm) in CD_2Cl_2. [b] δ (ppm) in CD_3CN. [c] δ (ppm) in DMF. [d] $\Delta\delta$ is defined as the difference between the chemical shift of the $H_{3,8}$ proton in the $M\cdot 9^{n+}$ complex (M = Cu, Zn; n = 1, 2) and the chemical shift of this same proton in the $M\cdot 8^{n+}$ complex (M = Cu, Zn; n = 2, 4). [e] The compound **7** decomposes in DMF and in DMSO at 110 °C; below this temperature **7** is insoluble.

Preparation of the Silver(I) Complex $\mathbf{Ag_2 8^{2+}}$. One hundred milligrams (0.502 mmol) of $AgBF_4$ dissolved in 40 mL of toluene was added at room temperature to a stirred suspension of **8** (120 mg, 0.600 mmol) in 80 mL of CH_2Cl_2.

The reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After stirring, the solution was clear and colorless. After standing 2 h in the dark, white crystals appeared in the solution. They were filtered on paper, washed with 25 mL of toluene, and dried in vacuum: yield 142 mg (99%).

$\mathbf{Ag_2{\cdot}8^{2+}{\cdot}2BF_4^-}$: colorless crystals (mp 288 °C, dec); ^1H NMR (see Table IV); MS, calculated 2312.8, found 2311.9. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Ag_2B_2F_8{\cdot}CH_2Cl_2{\cdot}H_2O$: C, 61.86; H, 4.32; N, 4.47. Found: C, 61.84; H, 4.31; N, 4.37.

Preparation of the Zinc(II) Complex $\mathbf{Zn_2{\cdot}8^{4+}}$. One hundred eleven milligrams (0.300 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ in 30 mL of EtOH was added with stirring at room temperature to a suspension of **8** (100 mg, 0.050 mmol) in CH_2Cl_2–CH_3CN (40 mL, 40 mL).

The reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After stirring for 24 h, the reaction mixture was clear and almost colorless. After evaporation of the solvents, the pale yellow solid obtained was washed with 200 mL of H_2O and filtered on a sintered glass: yield 98 mg (78%). The complex could be recrystallized from CH_3CN–toluene, affording an analytical sample.

$\mathbf{Zn_2{\cdot}8^{4+}{\cdot}4ClO_4^-}$: colorless crystals (mp 174 °C, dec); ^1H NMR (see Table IV); MS, calculated 2439.4, found 2439.1. Anal. Calcd for $C_{128}H_{104}N_8O_{36}Zn_2Cl_4$: C, 60.33; H, 4.10; N, 4.41. Found: C, 60.32; H, 4.21; N, 4.40.

Preparation of the Cobalt(II) Complex $\mathbf{Co_2{\cdot}8^{4+}}$. Sixty milligrams (0.164 mmol) of $Co(BF_4)_2{\cdot}6H_2O$ dissolved in 10 mL of EtOH was added with stirring at room temperature to a suspension of **8** (150 mg, 0.075 mmol) in 80 mL of CH_3CN.

The reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After stirring for 2 h, a bright orange color appeared, and the solution was clear; 80 mL of EtOH was then slowly added to the solution: a dark orange solid began to precipitate. Crude $Co_2{\cdot}\mathbf{8}^{4+}$ was filtered after 24 h and dried in vacuum: yield 120 mg (65%).

$\mathbf{Co_2{\cdot}8^{4+}{\cdot}4BF_4^-}$: brown crystals (mp 293 °C, dec); MS, calculated 2388.6, found 2388.9. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Co_2B_4F_{16}{\cdot}CH_2Cl_2{\cdot}2H_2O$: C, 59.66; H, 4.23; N, 4.31. Found: C, 59.63; H, 4.24; N, 4.32.

Preparation of the Nickel(II) Complex $\mathbf{Ni_2{\cdot}8^{4+}}$. One hundred eighty milligrams (0.049 mmol) of $Ni(BF_4)_2{\cdot}6H_2O$ in 45 mL of EtOH was added with stirring at room temperature to a suspension of **8** (150 mg, 0.075 mmol) in 90 mL of CH_3CN. The reaction was monitored by TLC (SiO_2, Kieselgel 60, 10% MeOH in CH_2Cl_2). After stirring for 72 h, the pale green reaction mixture still contained undissolved ligand **8**, and no further evolution was observed. The solvents were evaporated, and crude $Ni_2{\cdot}\mathbf{8}^{4+}$ was washed with 150 mL of H_2O and filtered on a sintered glass: yield 90 mg (49%). The complex could be recrystallized from CH_3CN–MeOH, affording an analytical sample.

$Ni_2{\cdot}\mathbf{8}^{4+}{\cdot}4BF_4^-$: pale yellow crystals (mp 277 °C, dec); MS, calculated 2388.1, found 2387.2. Anal. Calcd for $C_{128}H_{104}N_8O_{16}Ni_2B_4F_{16}{\cdot}MeOH{\cdot}H_2O$: C, 61.36; H, 4.39; N, 4.44. Found: C, 61.31; H, 4.33; N, 4.47.

Acknowledgment. We thank the financial contribution of the CNRS. Discussions with Dr. Jean-Marc Kern are also gratefully acknowledged as well as the Strasbourg mass spectroscopy group.

Isolation and First Structural Characterization of Dimethyl Sulfide Solvates of Phenyllithium, Phenylcopper, and Lower and Higher Order Lithium Phenylcuprate Reagents

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Abstract: The use of dimethyl sulfide as a solvent for organocopper reagents has allowed the first X-ray structure determinations of crystalline materials isolated from the addition of phenyllithium, in various ratios, to cuprous bromide in neat dimethyl sulfide. Upon removal of the insoluble lithium bromide, solutions of the 1:1 mixture yield crystals of $[Cu_4Ph_4(SMe_2)_2]$ (**1**). Its structure has a rhombus of four coppers that are edge-bridged by phenyl groups perpendicular to the Cu_4 plane and displays both long and short Cu⋯Cu diagonal distances of 4.101 (2) and 2.717 (2) Å, respectively. Two equivalents of LiPh with CuBr affords the species $[Li_2Cu_2Ph_4(SMe_2)_3]$ (**2**), an aggregate of two $[CuPh_2]^-$ moieties bridged by two Li^+ ions which are solvated by one and two SMe_2 groups. Treatment of CuBr with 3 equiv of LiPh produces the higher order cuprate $[Li_3(CuPh_2)(CuPh_3)(SMe_2)_4]$ (**3**). The first X-ray structural determination of such a species shows it to be an aggregate of $CuPh_2^-$ and $CuPh_3^{2-}$ moieties that are bridged by three Li^+ ions and solvated by four SMe_2 groups. A 10% excess over 3 equiv (3.3 equiv of LiPh per CuBr) does not give the all-trigonal higher order cuprate. Instead the larger aggregate, $[Li_5(CuPh_2)_3(CuPh_3)(SMe_2)_4]$ (**4**), is obtained. The structure of the phenyllithium precursor $[Li_4Ph_4(SMe_2)_4]$ (**5**) was also determined and found to be tetrameric, with one set of alternating corners of a cube occupied by $Li(SMe_2)$ and the other set of corners occupied by triply-bridging phenyls. It is the first structure of an organolithium thioether solvate complex that was crystallized from a thioether. The results demonstrate that it is possible to isolate higher order cuprates as crystalline materials from Me_2S solutions. Furthermore, the X-ray data are consistent with previously reported ^{13}C NMR solution studies that indicated the presence of **1**, **2**, **3**, and **5** in solution. In addition, structural relationships between LiPh, CuPh, $LiCuPh_2$, and the higher order phenyl cuprates have now been established which show that the ions $[CuPh_2]^-$ and $[CuPh_3]^{2-}$ are the dominant structural components in the cuprates when crystallized from Me_2S. A possible explanation for the lack of formation of certain higher order cuprates in conventional ether solvents is also provided.

The widespread use of neutral organocopper (CuR) or diorganocuprate (usually written as $LiCuR_2$ or variations thereof) reagents in organic synthesis has led to considerable interest in their structures. Neutral organocopper compounds have been known since 1923,[1] and cuprate species were first reported in 1952.[2] Subsequently, they were introduced as reagents in organic synthesis in 1966[3] and 1967.[4] Their reactions have been extensively investigated from the organic–synthetic viewpoint, and this work has been well reviewed.[5] Inquiry into the detailed

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