Synthesis of Macrocyclic Phenanthrolines with Exotopic Binding Sites. Probing Their Complexation Behavior with Copper(I) and Iron(II)

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Dedicated to Prof. Dr. F. Vögtle on the Occasion of his 60th Birthday

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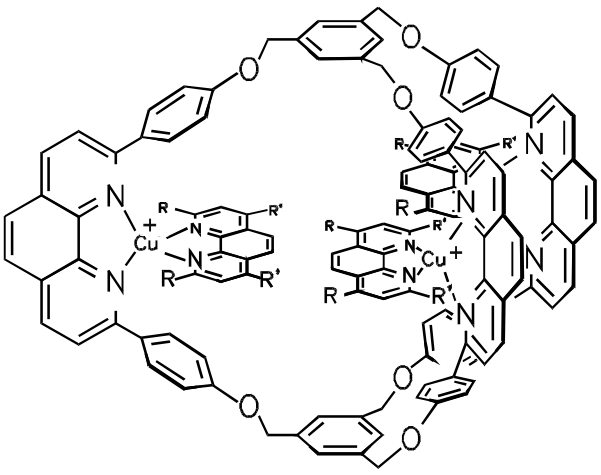
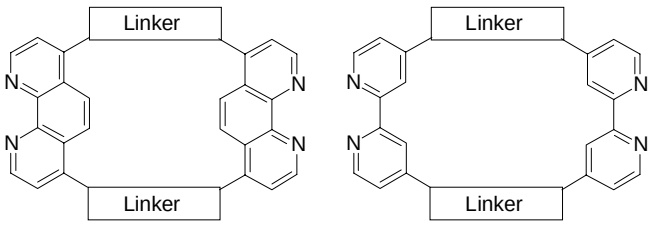
Abstract. Starting from 4,7-dichlorophenanthroline (**1**) a synthetic approach is developed to novel macrocyclic mono- and bisphenanthrolines (**5a**–**d**, **6a**–**d**) with exotopic binding sites. As these coordinating compounds are characterized by a flexible spacer unit, their utility as ligand for the construction of oligomeric, dendritic and box-like structures in the presence of copper(I) and iron(II) is evaluated. Spectroscopic data suggest that with copper(I) the [1+1] adduct $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$ is formed.

During recent years macrocyclic phenanthrolines [1] with endotopic coordination sites have attracted a lot of attention due to their key role in the formation of catenanes [2], rotaxanes [3], concave reagents [4] and molecular knots [5]. In addition, a macrobicyclic trisphenanthroline with endotopic binding sites was used by Vögtle *et al*. [6] to construe an endoreceptor the interior of which could be tailored through formation of three bisheteroleptic copper(I) phenanthroline complexes.



In contrast, macrocyclic bis- or oligophenanthrolines with exotopic bisimine sites of type **A** were described for the first time recently [7], while macrocycles containing exotopic bipyridines (such as **B**) have been reported from several laboratories [8].



We have become interested in the coordination chemistry of macrocyclic bisphenanthroline ligands **A** because of their potential for the convergent construction of redox active oligomers **C** (similar to oligomers prepared by Hosseini, Rehahn or Constable [9]), dendritic building blocks **D**, cubes **E** (resembling the cylindrical or pseudo-rotaxane structures by Lehn [10]), and fascinating nanotubes **F**. All these structures should be readily accessible through the simple self-assembly of three reactants: i) Cu^+ as coordinating metal ion with a tetrahedral complex geometry, ii) type **A** phenanthroline ligands, and if necessary iii) linearly connected 3,8-bis(oligo)phenanthrolines (for **E**, **F**).

The construction of such structures, however, relies decisively on a simple synthetic access to macrocyclic 4,7-disubstituted phenanthrolines **A** that is described in the following [7].

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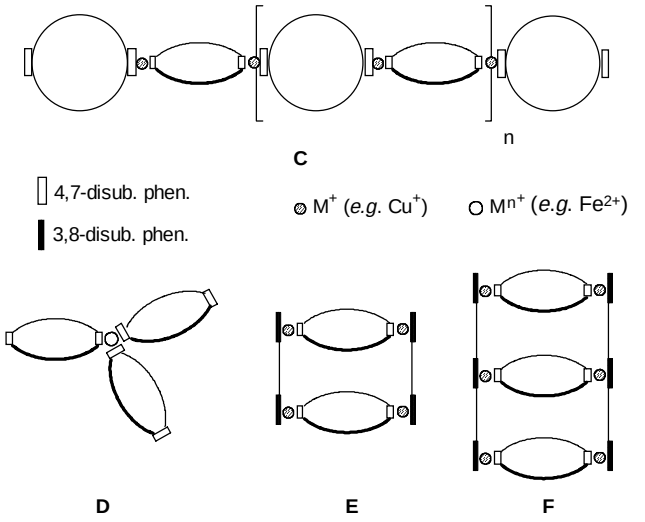
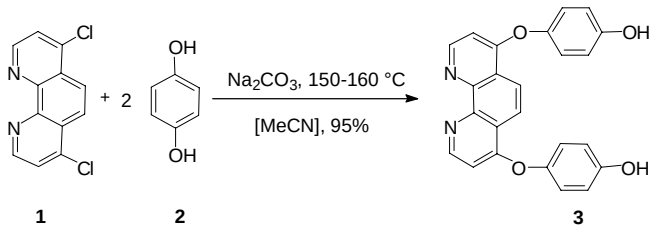


Scheme 1 Macrocyclic bisphenanthrolines with exoditopic binding sites as versatile building blocks in metallosupramolecular chemistry for the construction of oligomers (**C**), dendritic structures (**D**), cubes (**E**) or nanotubes (**F**).

Results and Discussion

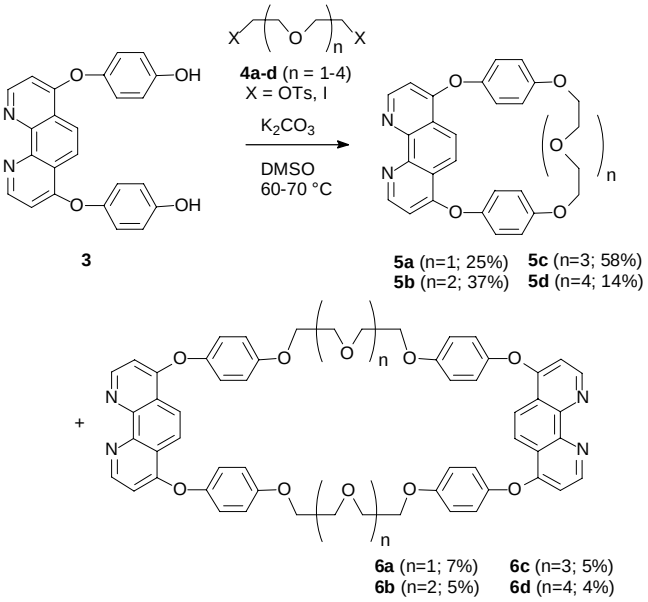
Macrocyclization

As a key building block for the desired oligophenanthroline macrocycle **A** we have prepared the bis(4-hydroxyphenoxy)-phenanthroline (**3**) because the *para*-hydroxy groups in **3** should be ideally suited for follow-up functionalizations. The aromatic hydroquinone group reduces the degree of rotational freedom that was expected to facilitate the construction of the macrocycle.



Importantly, reaction conditions as used earlier for the reaction of 4,7-dichlorophenanthroline (**1**) [11] with *p*-hydroxyanisole [12] could not be applied for the reaction of **1** with **2** (melted phenol). Instead **3** was readily prepared from **1** in presence of a large excess of *p*-hydroquinone and sodium carbonate as base in dry acetonitrile. Heating this mixture under nitrogen atmosphere at 150 – 160 °C in a sealed glass tube for 6 h led to the nearly quantitative formation of **3** (95%). Phenanthroline **3** turned out to be highly insoluble and could be isolated by filtration of the reaction mixture. After thoroughly rinsing the crude product with water to remove salts and hydroquinone residues recrystallization from ethanol yielded **3** in analytically pure form.

In order to develop an efficient and high-yield route for the preparation of the different macrocycles starting from phenanthroline **3** and various ditosylates/diiodides **4**, batch cyclizations as well as high-dilution procedures, which had already successfully been used for the synthesis of crown ether-type macrocycles by other groups [13, 14] were investigated. The optimization of reaction conditions was undertaken with **3** and **4c** (X = I) as reagents, varying the reaction time, base, solvent and conditions. The results, obtained by NMR- and mass analysis of the crude product mixture, are depicted in table 1.



When using sodium carbonate as base (entry II) or adding the coupling unit **4c** (X = I) very slowly within 4 days (entry IV), no macrocyclic products could be obtained. The highest yield of cyclized products (70 – 80%) was achieved when using the batch cyclization method (entry V). Under these conditions, DMSO seems to be a better solvent than DMF for the insoluble **3**. The reaction time plays an important role, as only a yield of 37% of **3** could be obtained when the reaction was stopped after 2 days. Similar results were obtained with cesium or potassium carbonate as base. Furthermore, the temperature control proved to be decisive for the yield of macrocyclic products. Temperatures above 80 °C led to a high amount of polymers, whereas at 50 °C or lower, the reaction was not complete. In the optimized procedure, which was finally used for the synthesis of the different macrocycles **5a**–**d** and **6a**–**d**, the starting phenanthroline **3** was first suspended in DMSO at 60 °C and then a slight excess of potassium carbonate and the coupling unit **4** was added. The mixture was then heated for **4** days prior to work-up.

The [1+1]-macrocycles **5a**–**c** with chain lengths of n = 1–3 could be obtained in increasingly good yields

Table 1 Various reaction conditions for the preparation of macrocycles **5c** and **6c**

Entry	Solvent	base [a])	temperature/reaction time	total product yield (%)	yield (%) **5c** and **6c**
I [b])	DMF	Cs_2CO_3 (1.5 eqs.)	100 °C/2 h addition, 22 h	50	ca. 20
II [b])	DMF	Na_2CO_3, (excess)	100 °C/2 h addition, 22 h	25	0
III [c])	DMF	Cs_2CO_3 (2 eqs.), K_2CO_3 (4 eqs.)	60 °C/2 d addition, 2 d	40	**5c** : 25, **6c**: 8
IV [c])	DMSO	Cs_2CO_3 (2 eqs.), K_2CO_3 (4 eqs.)	65 °C/4 d addition, 1 d	71	0
V [c])	DMSO batch	K_2CO_3 (8 eqs.)	65 °C/4 d	85	**5c**: 58, **6c**: 5

[a]) Equivalents of base per hydroxy group of **3**. [b]) coupling unit: ditosylate **4c (**X = OTs). [c]) Coupling unit: diiodide **4c** (X = I).

of 25–58%, whereas the product with n = 4 (**5d**) could only be isolated in a yield of 14%. The bisphenanthroline macrocycles **6a**–**d** were afforded in low yields of 4–7%. The template effect of the potassium ions seems to play an important role in product formation, as macrocycles with n = 4 are no longer favored, and uncyclized side products are isolated in higher yields. For the isolation of the products, it was advisable to wash the mixture with hexane to remove unpolar residues. As expected for 4,7-disubstituted phenanthrolines liquid chromatography had to be carried out on deactivated silica gel, but still the macrocyclic phenanthrolines were eluted extremely slowly affording always a mixture of **5** and **6**. While for most cases we had to separate the mono- and bisphenanthroline macrocycles by preparative size exclusion chromatography, the isolation of pure **5c** and **6c** was readily achieved by dissolving the mixture in dichloromethane. Upon concentrating the solvent bisphenanthroline macrocycle **6c** precipitated in a yield of 5%, while the monophenanthroline product **5c** was isolated (58%) by extracting the residue with boiling ethyl acetate.

Characterization of the Macrocycles

The products could be identified convincingly by NMR and electrospray mass spectroscopy. The ^{1}H NMR spectra of the mono- and bisphenanthroline macrocycles **5** and **6** differ characteristically. For example, the signal for the 5,6-phenanthroline protons in **5** typically appears 0.15 ppm downfield from that of bisphenanthroline **6**, while the 3,8-protons experience an opposite shift, as demonstrated for **5c** and **6c** in Figure 1. The sharp signals in both **5c** and **6c** indicate that rotation about single bonds is not restricted proposing that both structures are rather flexible.

Furthermore, the structure assignment of the [1+1] *vs*. [2+2] products was supported convincingly by ES-MS (electrospray mass spectrometry). The bisphenanthroline macrocycles **6** invariably display peaks for both the mono- and bisprotonated species $[M+H]^+$ and $[M+2H]^{2+}$, while the monophenanthrolines **5** only exhibit signals for the monoprotonated species $[M+H]^+$. In order to additionally confirm the assignment, the isotopic distribution (figure 2) was calculated for both isomers and was found to be in accordance with the experimental one (see in table 2).

Oligomeric Copper(I) Complexes with Bisphenanthroline (**6c**)

To probe whether the construction of an oligomeric framework of type **C** is possible the macrocyclic bisphenanthroline **6c** with its two chelating sites was cho-

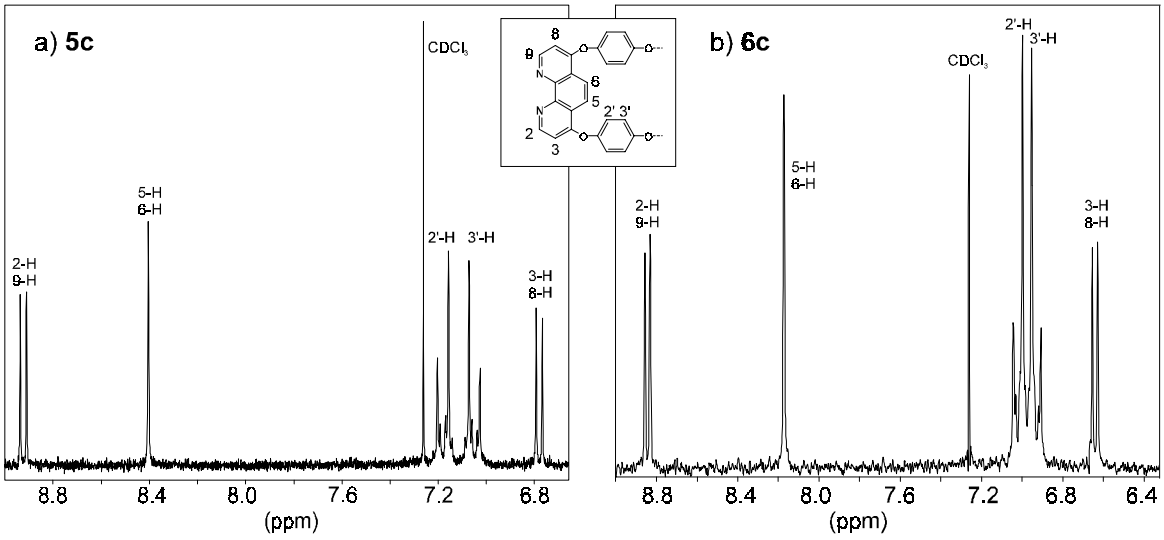


Fig. 1 Characteristic ^{1}H NMR absorptions (250 MHz, $CDCl_3$) in the aromatic region of the macrocyclic products **5c** and **6c**

Table 2 Calculated and detected isotopic distribution (*m/z*) for the molecular ions $[M+H]^+$ for mono- and $[M+H]^+$ and $[M+2H]^{2+}$ for bisphenanthroline macrocycles with ion intensities (%) in brackets

	Calcd.: $[M+H]^+$	Found:	Calcd.: $[M+2H]^{2+}$	Found:
6a	933.31 (100)	933.5 (100)	467.16 (100)	467.2 (100)
	934.32 (65)	934.5 (59)	467.66 (65)	467.7 (76)
	935.32 (23)	935.5 (17)	468.17 (23)	468.3 (27)
	936.32 (6)	936.6 (4)	468.67 (6)	468.8 (8)
5d	599.24 (100)	599.3 (100)		
	600.24 (39)	600.4 (32)		
	601.25 (9)	601.4 (8)		
	602.25 (2)	602.5 (2)		
6d	1197.47 (100)	1197.7 (100)	599.24 (100)	599.2 (100)
	1198.47 (79)	1198.7 (83)	599.74 (79)	599.8 (82)
	1199.48 (34)	1199.7 (58)	600.24 (34)	600.3 (28)
	1200.48 (10)	1200.8 (11)	600.74 (10)	600.9 (7)

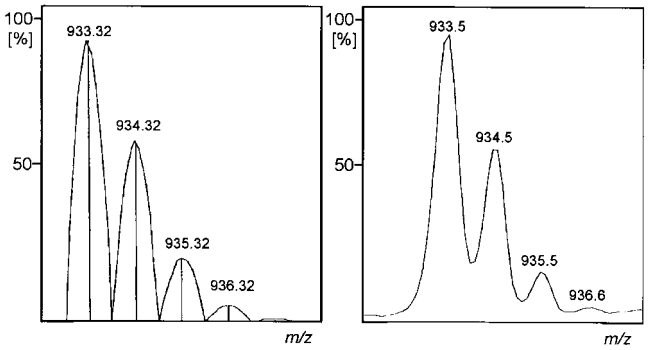
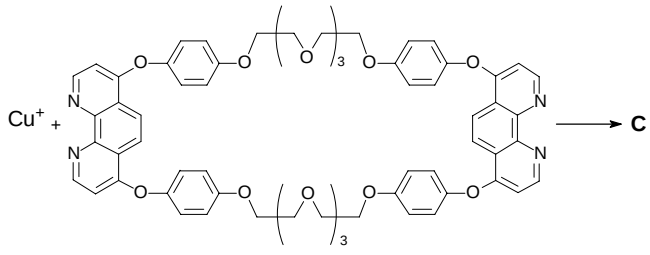


Fig. 2 Isotopic distribution pattern (*m/z*) according to the ES-MS investigation for the macrocycle **6a** (only the $[M+H]^+$ region); calculated (left) and experimental (right) spectra.

sen as a model substrate to study the coordination behavior of cyclic bisexotopic ligand with copper(I) ions (1:1).



6c

When mixing under an inert atmosphere in CD_2Cl_2 one equivalent of **6c** and $[Cu(MeCN)_4]BF_4$ immediately a red solution formed, indicative of the formation of a bisphenanthroline copper(I) complex. In line with this finding, the corresponding ^1H NMR spectrum displayed shifts of the phenanthroline signals characteristic of a bisphenanthroline copper(I) complex. However, after several minutes at room temperature the solution changed its color to yellow and consecutively to green, accompanied by a strong broadening of the ^1H NMR signals. Obviously, the bisphenanthroline complex formed immediately is prone to oxidation providing finally a copper(II) species.

Further insight into the coordination equilibria was obtained from an ES-MS analysis of such mixtures in acetonitrile–water. By mixing one equivalent of **6c** and copper(I) a molecular ion at *m/z* 1172.3 was detected. The isotopic pattern of the peak at *m/z* 1172.3 points to the formation of a multiply charged species with the composition of an oligomeric copper(I) complex, *i.e.* $[Cu(\mathbf{6c})]_n^{n+}$ ($n > 2$). Because of the limited resolution of our ES-MS instrument the exact magnitude of n in $[Cu(\mathbf{6c})]_n^{n+}$ could not be determined. After 60 minutes the mixture was analyzed again. This time, the ion $[Cu(\mathbf{6c})]_n^{n+}$ was only found in a small amount, whereas adducts of acetonitrile and/or water could be detected in high yields (Table 3).

Apparently, an oligomeric $[Cu(\mathbf{6c})]_n^{n+}$ can be generated by mixing equimolar amounts of **6c** and copper(I), however, it proves to be rather unstable and seems to react quickly to more stable adducts.

Coordination Chemistry of **6c** *with Iron(II)*

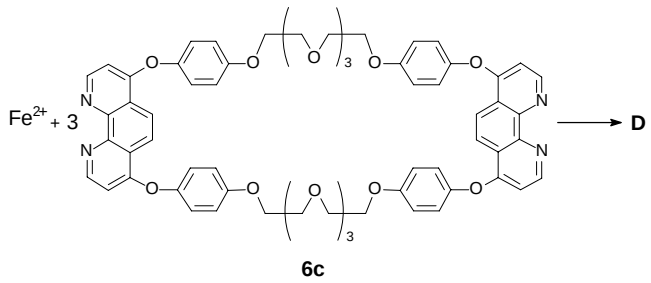
Since complexes of type **D** could open the way to dendritic or heterometallic structures, as reported by Balzani [15], we have investigated the reaction of iron(II) ions with ligand **6c**.

When we treated **6c** in dichloromethane with iron(II) sulfate in acetonitrile at various ratios, several product ions corresponding to complexes of the type $[Fe_m(\mathbf{6c})_n]^{2m+}$ ($m = 1-2$; $n = 1-3$) were detected by ES-MS analysis. The ion intensities as a function of the amount of iron(II) present were determined, and the results (in percent) are depicted graphically in figure 3.

It became obvious that even in the presence of a large excess of ligand **6c**, always a product mixture was obtained, and the desired complex $[Fe(\mathbf{6c})_3]^{2+}$ could only be found in traces. As a main product the complex $[Fe(\mathbf{6c})_2]^{2+}$ was detected in almost all cases. As the coordination of three phenanthroline units to the iron(II) center is usually energetically favored, we have to con-

Table 3 ES-MS-analysis of a mixture of equimolar amounts of **6c** and $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2; detected product ions, ion intensities (%) and assigned products.

Analysis	*m/z* of main product ion (100%)	*m/z* of further product ions
a) 1 min	1172.3 $[Cu(\mathbf{6c})]_n^{n+}$	1140.5 (30) $[Cu(\mathbf{6c})_2]^{2+}$; 1208.3 (5) $[Cu(\mathbf{6c})(H_2O)_2]_n^{n+}$
b) 60 min	1208.3 $[Cu(\mathbf{6c})(H_2O)_2]_n^{n+}$	1172.3 (50)$[Cu(\mathbf{6c})]_n^{n+}$; 1140.5 (10) $[Cu(\mathbf{6c})_2]^{2+}$; 676.7 (10) $[Cu_2(\mathbf{6c})(MeCN)_2(H_2O)_2]^{2+}$



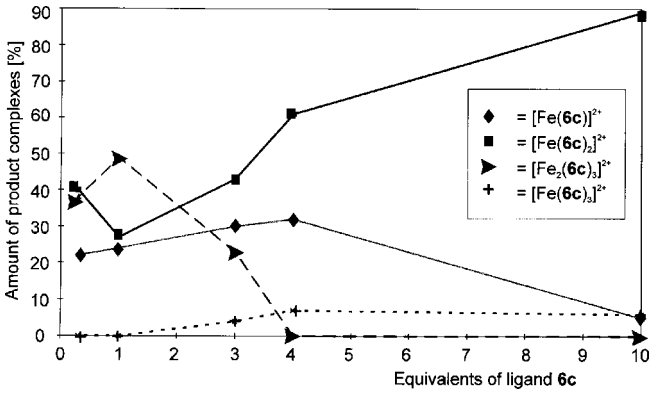
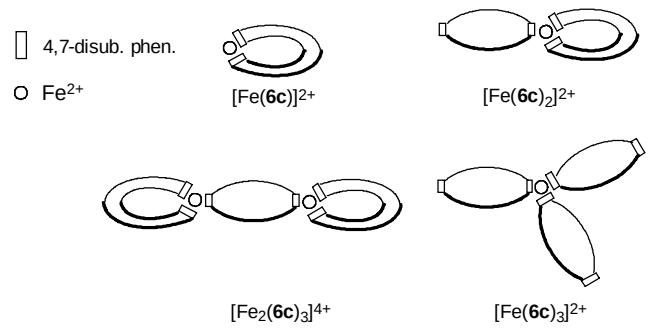


Fig. 3 Product ion distribution depending on the amount of **6c** (equivalents relative to iron(II)) present in the solution.

clude that in the main product the metal coordinates to both chelating units of one ligand **6c**. To facilitate the representation of the various options the corresponding complexes are illustrated schematically in Scheme 2.



Scheme 2 Schematic representation of compounds with various metal-to-ligand stoichiometries formed by coordination of the flexible bisphenanthroline macrocycle **6c** to iron(II).

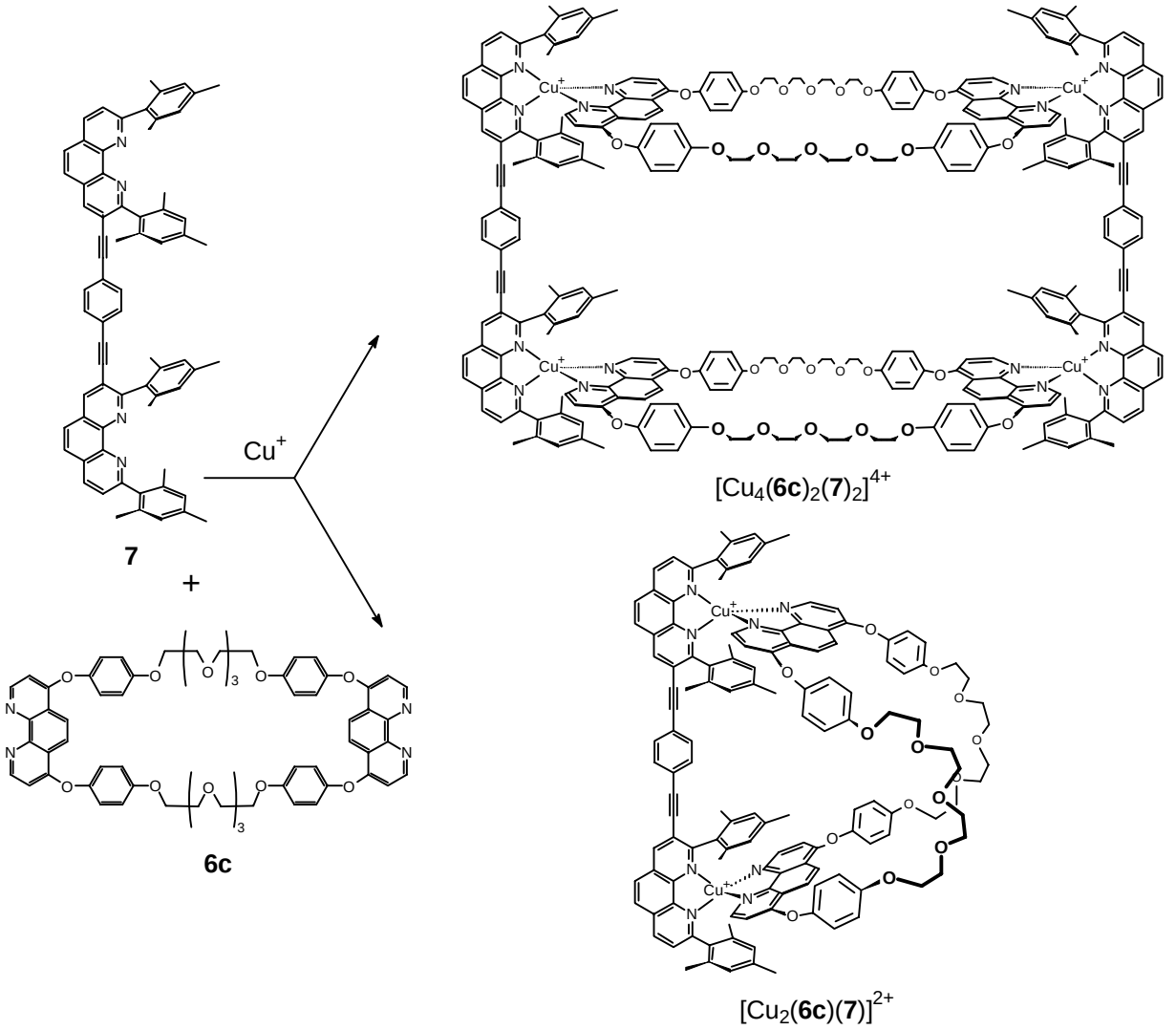
According to results obtained by Hosseini [9], the flexibility of ligands, such as **6c**, may therefore lead to a mixture of products. Force field calculations indeed reveal that the folding of one macrocycle **6c** is easily achieved to form the observed product complex $[Fe_2(\mathbf{6c})_3]^{4+}$.

Formation of a Heteroleptic Supramolecular Complex

We have recently reported about a strategy to selectively build heteroleptic bisphenanthroline copper(I) complexes by treating an unhindered phenanthroline with a phenanthroline carrying sterically crowded aryl substituents in 2,9-position [16]. The latter groups serve as a steric blocking unit to prevent the formation of the thermodynamically most stable homoleptic copper(I) complex carrying aryl groups in 2,9-position.

To probe our concept for the construction of redox active cubes of type **E**, the macrocyclic bisphenanthrolines **6** should simply be treated with the linear bisphenanthroline **7** containing the steric blocking unit. The latter has been made available in a multistep synthesis recently [17] from 3-bromophenanthroline [18]. When we treated equimolar amounts of **6c** and **7** at room temperature with two equivalents of $[Cu(MeCN)_4]PF_6$ in dichloromethane, immediately a red solution formed. After purification a red solid was obtained in 53% yield. Although the red color of the product clearly indicates the formation of a copper(I) bis-phenanthroline complex, there are still several options plausible. ES-MS-analysis shows a product ion at *m/z* 1095.5 corresponding to a complex of type $[Cu_{2n}(\mathbf{6c})_n(\mathbf{7})_n]^{2n+}$, which reduces the options to heteroleptic complexes, most likely the [1+1] adduct $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$ and the [2+2] adduct $[Cu_4(\mathbf{6c})_2(\mathbf{7})_2]^{4+}$. This is supported by the ^1H NMR analysis revealing conspicuous chemical shifts, *e.g.* the methyl protons of the mesityl rings experience a characteristic high-field shift (δ = 1.40 ppm) due to $\pi-\pi$ stacking interactions with the phenanthroline moiety of **6c**. Higher cyclic mixed oligomers are unlikely since copper(I) bisphenanthrolines are labile at room temperature disfavoring larger aggregates.

Several arguments finally support the proposal that compound $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$ was isolated: (1) The isotopic pattern (analogous to our earlier discussion, s. table 2) of the M^+ peak argues in favor of $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$. (2) Collision activated fragmentation in tandem MS experiments with 1095.5 as precursor ion led to product ions



at *m/z* 1171.9, 1019.6 and 540.9, corresponding to the complex fragments $[Cu(\mathbf{6c})]^+$, $[Cu(\mathbf{7})]^+$ and $[Cu_2(\mathbf{7})]^{2+}$ (figure 4), but no fragments were found conforming to $[Cu_4(\mathbf{6c})(\mathbf{7})_2]^{4+}$, $[Cu_2(\mathbf{6c})_2(\mathbf{7})]^{2+}$ and other fragments typical for the [2+2]adduct. (3) ROESY investigations provide strong interactions between the internal mesityl groups of **7** and the phenanthroline of **6c** in complex $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$, much stronger than the interactions between the external mesityl groups of **7** and the phenanthroline of **6c** (figure 5). This indicates that the phenanthroline unit of **6c** is tilted towards the internal mesityl group, in line with the steric requirements of a complex $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$. NMR shifts at the internal mesityl rings are equally different from those at the external mesityl rings supporting the above picture.

Model calculations using the MM^+ force field indeed indicate that ligand **6c** is flexible enough to coordinate twice to one molecule of **7**. Hence, it will be important for the formation of boxes of type **E** to use rigid exoditopic phenanthroline macrocycles, a work that is well progressed in our laboratories and that will be reported soon.

In conclusion, we have reported about the first preparation of exotopic and exoditopic phenanthroline macrocycles and their use in copper(I) and iron(II) complexes. Investigations on using these ligands in nonlabile complexes, such as with Ru(II), are in progress.

Generous financial support from the DFG and the Fonds der Chemischen Industrie is gratefully acknowledged.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200, AM-250 or DMX 600 instruments and calibrated with tetramethylsilane as an internal reference (TMS, δ = 0.0 ppm). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were recorded on a Perkin-Elmer 1605 series FT-IR-spectrometer. Elemental analyses were measured on a Carlo Erba

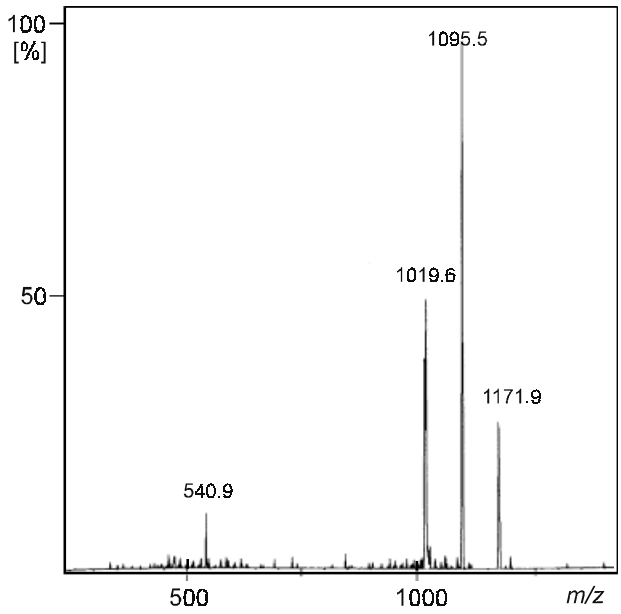


Fig. 4 Tandem MS experiment: collisionally activated decomposition of *m/z* = 1095.5 corresponding to $[Cu_{2n}(\mathbf{6c})_n(\mathbf{7})_n]^{2n+}$ (n ≥1).

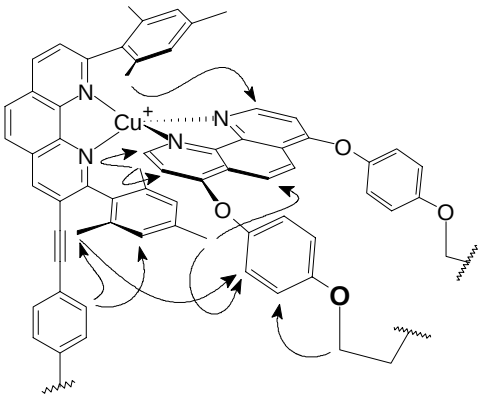


Fig. 5 Schematic representation of a fragment of $[Cu_2(\mathbf{6c})(\mathbf{7})]^{2+}$ with the most relevant through-space interactions derived from ROESY investigations.

Elemental Analyzer 1106. Melting points were determined by using a Mettler FP5.0. Electrospray (ES) MS spectra were recorded on a TSQ 7000 Triple-Quadrupol-Tandem-Mass spectrometer (Finnigan MAT) with Finnigan ESI-Interface. Data recording and evaluation was carried out using the ICIS 8.1 software package (Finnigan MAT). Preparative size exclusion chromatography was accomplished using a Kontron pump HPLC 422 on a polystyrene-divinylbenzene-copolymer column (Polymer Laboratories) 100 Å (600×25 mm, 10 µmm); solvent: $CHCl_3$ (5–10 ml min^{-1}).

4,7-Bis(p-hydroxyphenoxy)-1,10-phenanthroline (**3**)

A suspension of 4,7-dichlorophenanthroline (**1**) (504 mg, 2.02 mmol), *p*-hydroquinone (**2**) (3.38 g, 30.7 mmol) and anhydrous sodium carbonate (6.40 g, 60.0 mmol) in anhydrous acetonitrile (25 ml) was heated in an autoclave at 150–160 °C for 6 h. After cooling to room temperature the mixture was filtered and washed thoroughly with water until the filtrate remained colorless. The solid residue was dried and recrystallized from ethanol (95%) to furnish 750 mg (95%) of colorless needles, *m.p.* 280–290 °C (dec.). – ^{1}H NMR (200 MHz, d_6-DMSO): δ/ppm = 5.75 (s, 2H, O-H), 6.92 (d, 2H, Phen), 6.96 (d, 4H, Ar-H), 7.20 (d, 4H, ArH), 8.46 (s, 2H, Phen), 8.93 (d, 2H, Phen). – ^{13}C NMR (63 MHz, d_6-DMSO): δ/ppm = 106.3, 116.7, 119.1, 120.4, 122.0, 144.8, 146.7, 151.3, 156.4, 162.0. – IR: ν/cm^{-1} = 3278, 1589, 1508, 1261, 1231, 916.

$C_{24}H_{16}N_2O_4 \cdot H_2O$	Calcd.:	C 69.56	H 4.38	N 6.76
(414.12)	Found:	C 69.25	H 4.70	N 6.30.

Preparation of the Macrocycles Using the Batch-cyclization Method (General Procedure)

A mixture of 4,7-dichlorophenanthroline (**3**) (1.31 mmol), the coupling unit **4** (X = OTs) (1.33 mmol) [19, 20] and potassium carbonate (19.5 mmol) in anhydrous DMSO (50 ml) was heated for 4 days to 60–70 °C. The solvent was removed by distillation *in vacuo*, and the brown residue taken up in water and dichloromethane. The aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography (silica gel, dichloromethane : methanol : ammonia = 100:10:1). A product fraction containing both products **5** and **6** was obtained. These were separated by SEC (chloroform, flow: 10 ml min^{-1}; *p* = 13 bar).

4,7-(Epoxy[1,4]-benzenoxyethanoxyethan-oxy[1,4]-benzenoxy)-1,10-phenanthroline (**5a**) and *4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxy[1,4]-benzenoxy-[4,7]-endo-[1,10]-phenanthroline-oxy-[1,4]-benzenoxyethanoxyethanoxy-[1,4]-benzenoxy)-1,10-phenanthroline* (**6a**)

5a (25%) colorless solid; *m.p.* 132–133 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.97 (m, 4H, O–CH_2), 4.20 (m, 4H, O–CH_2), 6.73 (d, 2H, Phen), 6.96 (d, 4H, ArH), 7.13 (d, 4H, ArH), 8.35 (s, 2H, Phen), 8.86 (d, 2H, Phen). – ^{13}C NMR (63 MHz, $CDCl_3$): δ/ppm = 68.5, 70.4, 107.0, 116.6, 119.8, 121.6, 122.6, 147.6, 148.0, 151.5, 157.0, 163.0. – IR: ν/cm^{-1} = 2870, 1588, 1492, 1227, 1201, 1129, 912, 827.

$C_{28}H_{22}N_2O_5 \cdot 3.5H_2O$	Calcd.:	C 63.51	H 5.52	N 5.29
(529.19)	Found:	C 63.51	H 5.45	N 4.81.

6a (7%) colorless solid; *m.p.* 173–175 °C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.93 (m, 4H, O–CH_2), 4.10 (m, 4H, O–CH_2), 6.63 (d, 2H, Phen), 6.95 (m, 8H, ArH), 8.20 (s, 2H, Phen), 8.84 (d, 2H, Phen). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 66.3, 70.2, 106.3, 116.1, 116.7, 121.2, 122.0, 147.1, 147.3, 151.2, 156.5, 162.9.

ES-MS: $C_{56}H_{44}N_4O_{10}$ [M+H] Calcd.: 933.3 Found: 933.6
Isotopic distribution, see Table 2

4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxyethanoxy-[1,4]benzenoxy)-1,10-phenanthroline (**5b**) and *4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxyethanoxy[1,4]-benzenoxy-[4,7]-endo-[1,10]-phenanthroline-oxy-[1,4]-benzenoxyethanoxyethanoxyethanoxy-[1,4]-benzenoxy)-1,10-phenanthroline* (**6b**)

5b (37%) of a light brown solid; *m.p.* 104–105 °C. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.80 (s, 4H, O–CH_2), 3.92 (m, 4H, O–CH_2), 4.19 (m, 4H, O–CH_2), 6.75 (d, 2H, Phen), 7.02

(d, 2H, ArH), 7.14 (d, 2H, ArH), 8.36 (s, 2H, Phen), 8.89 (d, 2H, Phen). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 67.9, 69.8, 70.8, 106.5, 116.1, 119.4, 121.1, 122.1, 147.2, 150.9, 156.5, 162.4. – IR: ν/cm^{-1} = 2870, 1588, 1491, 1227, 1200, 1105, 912, 827, 730.

$C_{30}H_{26}N_2O_6 \cdot 2.5H_2O$	Calcd.: C 64.86	H 5.62	N 5.04
(555.21)	Found: C 64.55	H 5.50	N 4.72.

6b (5%) colorless solid; *m.p.* 197–200 °C (dec.). – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.76 (s, 4H, O–CH_2), 3.88 (m, 4H, O–CH_2), 4.16 (m, 4H, O–CH_2), 6.58 (d, 2H, Phen), 6.91 (s, 8H, ArH), 8.06 (s, 2H, Phen), 8.79 (d, 2H, Phen). – ^{13}C NMR (63 MHz, $CDCl_3$): δ/ppm = 68.2, 70.0, 71.6, 106.0, 116.7, 119.4, 121.3, 122.8, 146.9, 147.3, 151.0, 157.3, 162.5. – IR: ν/cm^{-1} = 2870, 1588, 1492, 1227, 1200.

$C_{60}H_{52}N_4O_{12} \cdot 4H_2O$	Calcd.: C 61.85	H 5.88	N 4.81
(1092.40)	Found: C 61.68	H 5.47	N 4.26.

4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxyethanoxy-ethanoxy[1,4]benzenoxy)-1,10-phenanthroline (**5c**) and *4,7-(Epoxy[1,4]-benzenoxyethanoxyethaoxyethanoxy[1,4]-benzenoxy-[4,7]-endo-[1,10]-phenanthroline-oxy-[1,4]-benzenoxyethanoxethanoxyethanoxyethanoxy-[1,4]-benzenoxy)-1,10-phenanthroline* (**6c**)

A suspension of **3** (400 mg, 1.02 mmol), **4c** (X = I) (460 mg, 1.10 mmol) and potassium carbonate (2.00 g, 15.0 mmol) in DMSO (30 ml) was brought to reaction. After workup and column chromatography the residue was taken up in a small amount of dichloromethane, thus precipitating a white solid (**6c**) that was filtered off and dried. After removing the solvent the filtrate was extracted with hexane and boiling ethyl acetate. The solid residue (**5c**) was dried.

5c (58%) of a yellowish solid; *m.p.* 91–92 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.72 (m, 8H, O–CH_2), 3.87 (m, 4H, O–CH_2), 4.15 (m, 4H, O–CH_2), 6.73 (d, 2H, Phen), 6.98 (d, 4H, ArH), 7.15 (d, 4H, ArH), 8.36 (s, 2H, Phen), 8.85 (d, 2H, Phen). – ^{13}C NMR (63 MHz, $CDCl_3$): δ/ppm = 68.0, 69.8, 70.7, 70.9, 106.6, 116.1, 119.5, 121.2, 122.2, 147.2, 147.7, 151.0, 156.6, 162.5. – IR: ν/cm^{-1} = 1506, 1490, 1227, 1200, 828.

$C_{32}H_{30}N_2O_7 \cdot 3.5H_2O$	Calcd.: C 62.23	H 6.04	N 4.54
(617.24)	Found: C 62.11	H 5.54	N 4.52.

6c (5%) colorless solid; *m.p.* 230 °C (dec.). – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 3.76 (m, 8H, O–CH_2), 3.92 (m, 4H, O–CH_2), 4.12 (m, 4H, O–CH_2), 6.64 (d, 2H, Phen), 6.93 (d, 4H, ArH), 7.00 (d, 4H, ArH), 8.17 (s, 2H, Phen), 8.84 (d, 2H, Phen). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 68.1, 69.7, 70.8, 70.9, 106.2, 116.0, 119.3, 121.0, 122.4, 147.3, 147.5, 150.9, 156.6, 162.4. – IR: ν/cm^{-1} = 1494, 1420, 1203, 836. – MS-DCI (70–100 eV): *m/z* (%) = 1109.8 (66.1), 555.4 (2.14).

$C_{64}H_{60}N_4O_{14} \cdot 2H_2O$	Calcd.: C 67.11	H 5.63	N 4.89
(1144.43)	Found: C 66.93	H 5.70	N 5.00.

4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxyethanoxy-ethanoxyethanoxy[1,4]benzenoxy)-1,10-phenanthroline (**5d**) and *4,7-(Epoxy[1,4]-benzenoxyethanoxyethanoxyethanoxy-ethaoxyethanoxy[1,4]-benzenoxy-[4,7]-endo-[1,10]-phenanthroline-oxy-[1,4]-benzenoxyethanoxethanoxyethanoxy-ethanoxyethanoxy-[1,4]-benzenoxy)-1,10-phenanthroline* (**6d**)

5d (14%) of a yellow oil. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.71 (m, 12H, O–CH_2), 3.91 (m, 4H, O–CH_2), 4.18 (m, 4H, O–CH_2), 6.77 (d, 2H, Phen), 7.02 (d, 4H, ArH), 7.16 (d, 4H, ArH), 8.40 (s, 2H, Phen), 8.91 (d, 2H, Phen). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 68.0, 69.8, 70.7, 70.9, 106.6, 116.1, 119.4, 121.2, 122.1, 147.4, 147.8, 151.0, 156.6, 162.4. – IR: ν/cm^{-1} = 1508, 1492, 1229, 1202, 841.
ES-MS: $C_{34}H_{34}N_2O_8$ [M+H] Ber.: 599.2 Gef.: 599.6.
Isotopic distribution, see Table 2.

6d (4%) of a colorless oil. – ^{1}H NMR (200 MHz, $CDCl_3$): δ/ppm = 3.62 (m, 12H, O–CH_2), 3.90 (m, 4H, O–CH_2), 4.11 (m, 4H, O-CH_2), 6.67 (d, 2H, Phen), 6.93 (d, 4H, ArH), 7.16 (d, 4H, ArH), 8.23 (s, 2H, Phen), 8.86 (d, 2H, Phen). – ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm = 68.7, 70.4, 71.2, 71.4, 71.6, 107.0, 116.7, 120.0, 121.8, 122.8, 148.0, 148.2, 151.6, 157.2, 163.0. – IR: ν/cm^{-1} = 1471, 1199, 840. – ES-MS: $C_{68}H_{68}N_4O_{16}$ [M+H] Ber.: 1198.4 Gef.: 1198.7.
Isotopic distribution, see Table 2.

Coordination Behavior of Compound 6c with Copper(I)

A solution of compound **6c** (10.0 mg, 9.0 μmol) in 0.7 ml of CD_2Cl_2 was thoroughly degassed under an inert atmosphere, and a degassed solution of $[Cu(MeCN)_4]BF_4$ (3.00 mg, 9 μmol) in 50 μl of acetonitrile was added. The mixture was examined by NMR-spectroscopy after 1 min and after 60 min. **6c** (1.0 mg, 0.9 μmol) was dissolved in 10 ml of dichloromethane. A solution of $[Cu(MeCN)_4]BF_4$ (0.3 mg, 0.9 μmol) in acetonitrile/water (9:1, 1 ml) was added, and the resulting mixture examined by ES-MS analysis after 1 min and after 60 min. The experiment was repeated. The detected product ions are shown in Table 3.

Coordination Behavior of Compound 6c with Iron(II)

Iron(II)sulfate-heptahydrate (10, 25, 33, 100 and 300 μml of a 90 mM solution in acetonitrile) was added to 1 ml aliquots of a solution of **6c** (10.0 mg, 9.0 μmol dissolved in 10 ml of dichloromethane). The resulting mixtures were examined by ES-MS spectroscopy. Product ions corresponding to structures $[Fe_m(\mathbf{6c})_n]^{2m+}$ (m = 1–2; n = 1–3) were detected. Additionally, adducts of type $[Fe_m(\mathbf{6c})_n(CF_3CO_2^-)]^{(2m-1)+}$ were found in cases where free coordination sites at the metal were still present, as the mass spectrometer contains residual traces of trifluoroacetic acid. The ion intensities of the molecular ions were determined, and their share in the total amount of ions was calculated (Table 4).

Table 4 Mass spectroscopic investigation of the products formed after mixing Fe(II) and **6c** in various amounts. Depicted are the relative ion intensities (%) belonging to one class of complex.[a–d)]

Fe(II): **6c**	$[Fe(\mathbf{6c})]^{2+}$ [a)]	$[Fe(\mathbf{6c})_2]^{2+}$ [b)]	$[Fe_2(\mathbf{6c})_3]^{4+}$ [c)]	$[Fe(\mathbf{6c})_3]^{2+}$ [d)]
1:10	5	89	–	6
1:4	32	61	–	7
1:3	30	43	23	4
1:1	24	27	49	–
3:1	22	40	38	–

[a)] $[Fe(\mathbf{6c})]^{2+}$ (582.6) + $[Fe(\mathbf{6c})(CF_3CO_2^-)]^+$ (1277.4). [b)] $[Fe(\mathbf{6c})_2]^{2+}$ (1136.6). [c)] $[Fe_2(\mathbf{6c})_3]^{4+}$ (860.0) + $[Fe_2(\mathbf{6c})_3(CF_3CO_2^-)]^{3+}$ (888.2). [d)] $[Fe(\mathbf{6c})_3]^{2+}$ (1690.8).

Box-type complex: $[Cu_2(6c)(7)](PF_6)_2$ or $[Cu_4(6c)_2(7)_2](PF_6)_4$

Compound **7** (14.6 mg, 15.3 μmol) was dissolved in dichloromethane (10 ml) under nitrogen and $[Cu(MeCN)_4]PF_6$ (11.4 mg, 32.0 μmol) added. After addition of the phenanthroline **6c** (17.0 mg, 15.3 μmol) the mixture was stirred at room temperature for an additional 30 min, and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane and precipitated through addition of hexane to yield 20 mg (53%) of a red solid. *m.p*. 234 °C (dec.). – ^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 1.40 (s, 12H, Ar–CH_3), 1.88 (s, 6H, Ar–CH_3), 1.89 (s, 6H, Ar–CH_3), 1.97 (s, 12H, Ar–CH_3), 3.68 (m, 16H, O–CH_2), 3.86 (m, 8H, O–CH_2), 4.21 (m, 8H, O–CH_2), 5.86 (s, 4H, ArH), 6.47 (s, 4H, ArH), 6.50 (s, 4H, ArH), 6.82 (d, 4H, Phen), 7.14 (d, 8H, ArH), 7.24 (d, 8H, ArH), 7.90 (d, 2H, Phen), 8.10 (d, 2H, Phen), 8.18 (d, 2H, Phen), 8.23 (d, 4H, Phen), 8.40 (s, 4H, Phen), 8.61 (s, 2H, Phen), 8.68 (d, 2H, Phen). – ^{13}C NMR (151 MHz, CD_2Cl_2): δ/ppm = 19.4, 20.2, 20.9, 21.6, 68.4, 70.0, 71.1, 71.3, 107.6, 116.8, 120.1, 122.2, 126.6, 127.4, 128.1, 128.6, 131.6, 137.5, 137.9, 149.5 [21]. – IR: ν/cm^{-1} = 2921, 2214, 1579, 1492, 1199, 842, 558. – ES-MS: $C_{134}H_{116}N_8O_{14}Cu_2$ Calcd. 1095.4 Found: 1095.5 or $C_{268}H_{232}N_{16}O_{28}Cu_4$ Calcd. 1095.6. – MS-MS experiment: (1095.5, 60 eV) Found: 1171.9 (28) [Cu(**6c**)]$^+$, 1019.6 (52) [Cu(**7**)]$^+$, 540.9 (12) [Cu_2(**7**)]$^{2+}$.

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