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Concave Reagents 36: Transition Metal Complexes With Concave 1,10-phenanthrolines*

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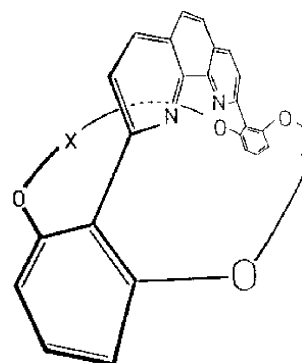
Complexes between concave 1,10-phenanthrolines **1** and transition metal ions (Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^+ , Cu^{2+} , Zn^{2+} , Ag^+ , Cd^{2+}) have been synthesized and characterized by various methods including UV titration, NMR spectroscopy, EPR spectroscopy, cyclic voltammetry, microanalysis and X-ray analysis. The concave 1,10-phenanthrolines **1** form 1:1 complexes with the metal ions while the complexes of analogous, but non-bimacrocyclic 1,10-phenanthrolines such as **2** and 2,9-dimethyl-1,10-phenanthroline exist in varying stoichiometries.

Keywords: Transition metal complex; Macrocycle; Redox-system; Concave ligands

1,10-Phenanthroline is a good ligand for transition metal ions in various oxidation states [1–6]. The nitrogen donor atoms interact with metal ions forming 3:1 or 2:1 complexes. Substituted 1,10-phenanthrolines such as 2,9-dimethyl-1,10-phenanthroline (neocuproine) or 2,9-diarylsubstituted 1,10-phenanthrolines [7–14] complex transition metal ions in an analogous way.

New concave ligands for transition metal ions are the 2,9-diaryl-substituted 1,10-phenanthrolines **1** and **2**. In **1**, the *ortho*-positions of the two aromatic bridgeheads are connected by polymethylene or polyether chains to form a bimacrocyclic system [13,14]. The geometry of these bimacrocycles resembles a light bulb, representing the nitrogen atoms of the 1,10-phenanthroline, in a lampshade [15–17], formed by the phenyl substituents and the side chains. Due to the concave shape of these

organic ligands, the transition metal ion is coordinated by only one ligand forming a 1:1 complex [14].



–X–

1a –(CH₂)₈–

1b –CH₂(CH₂OCH₂)₂CH₂–

1c –CH₂(CH₂OCH₂)₃CH₂–

2 –Me Me–

In these complexes, the metal ion is shielded from one side and should be accessible only from the other side (concept of concave reagents [15–17]). By this arrangement, stereo-, enantio-, chemo- or regioselectivities of reactions in which metal ions act as a catalyst should be determined by the concave organic ligand. A first successful application of these complexes led to enhanced stereoselectivities in transition metal catalyzed cyclopropanations [18–20], Diels-Alder reactions [21] and allylations [22].

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TABLE I Overview of complexes between transition metal salts MX_n and concave 1,10-phenanthrolines **1** and **2** investigated by various methods: M = microanalysis, U = UV titration, N = NMR spectroscopy, E = EPR spectroscopy, C = cyclovoltammetry, X = X-ray analysis. Most complexes had [1:1]-stoichiometry, stoichiometries other than [1:1] are indicated

Ligand	Mn ²⁺	Fe ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ⁺	Cu ²⁺	Zn ²⁺	Ag ⁺	Cd ²⁺
1a ·X ^{-*}	M(3:2) U+E‡	U†		U†	U†	U†				
1b ·X ^{-*}	MU	U		U	U	U	U	U¶	U§	
1c ·X ^{-*}	UC	MUNC	U	MUC	MUNC	UN¶#	M**U	U¶	U§	
1c ·I‡	MNEC			MU+EC	U+EC	C				
2 ·X ^{-*}	U†	M ^{††} (2:1) C	M¶	U†	U†	2:1 MN	M**X**	M§	M¶N¶¶	M§
2 ·I‡	M			M(3:1)		M**N**				

*Nf⁻ as counter ion unless stated otherwise. †Ref. [14]. ‡I⁻ as counter ion. ¶Cl⁻ as counter ion. §Trifluoroacetate as counter ion. ¶¶Tetrafluoroborate as counter ion. #Ref. [13]. **Br⁻ as counter ion. ††ClO₄⁻ as counter ion.

In this work, we have investigated the complex formation of **1** and **2** with first row transition metal ions (Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu⁺, Cu²⁺, Zn²⁺), and with Ag⁺ and Cd²⁺. For the characterization of the complexes, various techniques in solution (UV titration, NMR spectroscopy, EPR spectroscopy, cyclovoltammetry) and in the solid state (microanalysis, X-ray analysis) can be used. An overview of the investigated complexes and the analytical techniques used in each case is given in Table I.

The solid metal ion complexes were synthesized by reaction of the organic ligands **1** and **2** with transition metal salts in dry, polar aprotic solvents at room temperature. Many complexes could be obtained analytically pure by recrystallization in varying yields. In many cases, metal nonafluorobutanesulfonates have been used [14]. This counter ion will be abbreviated as Nf⁻.

INVESTIGATIONS IN SOLUTION

UV Titrations

The formation of complexes between concave 1,10-phenanthrolines **1** and transition metal salts, especially nonafluorobutanesulfonates has been

investigated in acetonitrile. Association constants K_{assoc} for 1:1 complex formation have been calculated from UV titration data. The homogeneous change in the titration spectra ask for only two absorbing species, the ligand and the complex. Nevertheless, some stoichiometries have been checked by Job plots [23], and they are supported by microanalyses (see below) in most cases. Only for **1a**·MnI₂, a 3:2 stoichiometry was found in the crystalline state. This asks for a thorough control by Job plots at different wavelengths and concentrations. Unfortunately, the Job plots for **1a**·MnI₂ at a total concentration of 0.25 mM only showed a broad plateau between 70:30 and 45:55 (**1a**:MnI₂) instead of a maximum at 1:1 stoichiometry (see Table II for data at 320 nm).

At first glance, the finding of a plateau instead of a maximum argues against the 1:1 stoichiometry. But the plateau is in agreement with a 1:1 stoichiometry if the relatively small binding constant K_{assoc} for **1a**·MnI₂ is taken into account (determined by UV titration and confirmed by EPR measurements, see below). Using this association constant and assuming 1:1 stoichiometry, the observed plateau also can be calculated (see Table II). The plateau therefore is in accordance with a 1:1 stoichiometry! In principle at much higher concentrations, the ratio between

TABLE II Job plot data for the complex formation between **1a** and MnI₂ measured at 320 nm in acetonitrile at a total concentration of 0.25 mM. At the concentrations used, the complex is partially dissociated*. Assuming a 1:1 stoichiometry, the concentrations of all species in solution and their respective absorbances were calculated†. The resulting absorbances E_{320} (calculated) are compared to the measured values E_{320} (measured)

Ratio (1a :MnI ₂)	E_{320} (measured)	E_{320} (calculated)†	[Mn ²⁺]† 10 ⁻⁵ M	[Mn ²⁺ · 1a]† 10 ⁻⁵ M	[1a]† 10 ⁻⁵ M
100:0	0.77	0.77	–	–	25.0
70:30	1.09	1.06	1.1	6.4	11.1
65:35	1.12	1.09	1.6	7.2	9.1
60:40	1.19	1.10	2.2	7.8	7.2
55:45	1.21	1.10	3.0	8.25	5.5
50:50	1.08	1.08	4.1	8.4	4.1
45:55	1.00	1.02	5.5	8.25	3.0
40:60	0.94	0.95	7.2	7.8	2.2

* $K_{\text{assoc}} = 10^{4.7}$, Ref. [14]. † From the absorbance of the solution containing only the concave 1,10-phenanthroline **1a** (100:0), the absorbance coefficient for **1a** can be calculated: $\epsilon_{320}(\mathbf{1a}) = 3080$. Using $K_{\text{assoc}} = 10^{4.7}$ for the complex formation between **1a** and Mn²⁺, the concentrations of [Mn²⁺], [Mn²⁺·**1a**] and [**1a**] have been calculated. At 50:50 for [**1a**] = 4.1×10^{-3} M, the fraction of the absorbance of the free concave ligand **1a** can be calculated to be $E_{320}(\mathbf{1a}) = 0.13$. Thus, the difference to the measured value $1.08 - 0.13 = 0.95$ results from the absorbance of the complex $E_{320}(\text{Mn}^{2+}\cdot\mathbf{1a})$. With [Mn²⁺·**1a**] = 8.4×10^{-5} M and $E_{320}(\text{Mn}^{2+}\cdot\mathbf{1a}) = 0.95$, $E_{320}(\text{Mn}^{2+}\cdot\mathbf{1a}) = 11300$ can be calculated. The absorbance of Mn²⁺ is negligible at 320 nm. Therefore, E_{320} (calculated) can be calculated from the ϵ_{320} values and from the concentrations as the sum of $E_{320}(\mathbf{1a})$ and $E_{320}(\text{Mn}^{2+}\cdot\mathbf{1a})$.

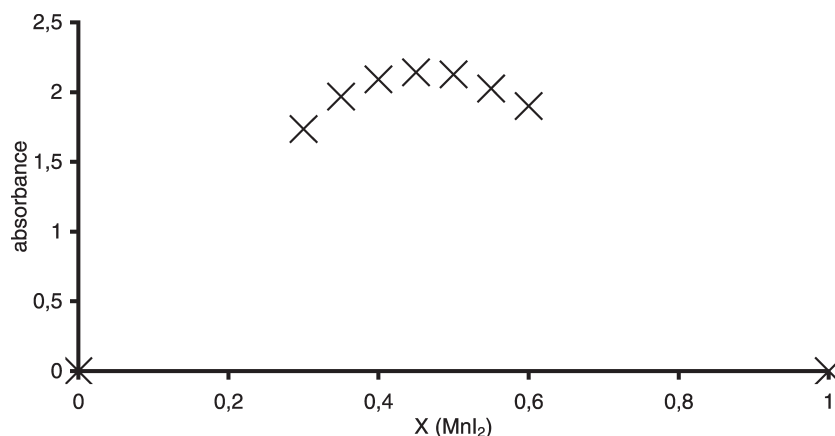


FIGURE 1 Job plot for the complex formation between **1a** and MnI_2 at 350 nm in acetonitrile at a total concentration of 1 mM plotted against the molar fraction X of MnI_2 . Each absorption has been corrected by $(1 - X)E_{350}(\mathbf{1a})$.

complex and free ligand should become larger and the plateau should vanish. Unfortunately for solubility reasons, the Job plot cannot be carried out at very high concentrations. But a second set of experiments has been carried out at a total concentration of 1 mM at 350 nm.† Indeed, the plateau vanishes and a maximum is now found at ca. 55:45 (see Fig. 1). But even at this higher total concentration some free ligand **1a** is still present and responsible for the shift of the maximum from 50:50 to ca. 55:45; for example at 50:50, $[\mathbf{1a}] = 9.0 \times 10^{-5} \text{ M}$ and $[\text{Mn}^{2+} \cdot \mathbf{1a}] = 41.0 \times 10^{-5} \text{ M}$.

Therefore association constants K_{assoc} have then been calculated from the UV titrations for 1:1 stoichiometries. In most cases, $\log K_{\text{assoc}} > 6.5$ was observed. Due to the applied concentrations, exact values can only be determined up to $\log K_{\text{assoc}} = 6.5$. Smaller constants were found for **1a** containing octamethylene chains which cannot coordinate to the metal ion [14]. Therefore, for Zn^{2+} and Ag^+ , the complex formation has only been measured with **1b** and **1c**. In Table III, these data are compared with the K_{assoc} values for other metal salt complexes measured in previous work [14]. The smaller concave ligand **1b** forms less stable complexes than the larger **1c** indicating the importance of steric interactions.

The 2,9-diaryl-1,10-phenanthroline **2** and 2,9-dimethyl-1,10-phenanthroline (neocuproine) also bind transition metal ions well. Due to the smaller sterical hindrance of these ligands near the metal binding site, 1:1 complexes have not been found in all combinations [14].

EPR Measurements

Complexes with paramagnetic metal ions possess unpaired electrons. Therefore, EPR measurements of three transition metal salts (MnI_2 , CoI_2 and NiI_2) and their complexes (**1a**· MnI_2 , **1c**· MnI_2 , **1c**· CoI_2 and **1c**· NiI_2) have been carried out at room temperature in acetonitrile.

The ligands **1a** and **1c** alone showed no EPR resonances as expected. For MnI_2 ($g = 2.0105$, $A_{\text{Mn}^{2+}} = 95.8$), CoI_2 ($g = 2.1054$, $A_{\text{Co}^{2+}} = 94.6$), and NiI_2 ($g = 2.009$, $A_{\text{Ni}^{2+}} = 96.1$) 6 lines were observed as expected (spin $I = 5/2$). In combination with ligand **1c**, however, the signals vanished.

Titration of MnI_2 with the concave ligands **1a** and **1c** were carried out in acetonitrile at 20°C and followed by EPR. Stepwise addition of the ligand led to a decrease of the EPR signals (Fig. 2) probably

TABLE III Logarithms of association constants $\log K_{\text{assoc}}$ for the complex formation between transition metal salts and concave 1,10-phenanthrolines **1b** and **1c** in acetonitrile

	MnNf_2^*	FeNf_2^*	FeNf_3^*	CoNf_2^*	NiNf_2^*	CuNf^*	CuNf_2^*	ZnCl_2	$\text{Ag}(\text{OOCFF}_3)$
1b	≥ 7	4.6	–	≥ 7	> 6.5	5.1	–	4.7	> 6.5
1c	≥ 7	> 6.5	> 6.5	≥ 7	> 6.5	> 6.5	5.6	5.0	≥ 7

*Ref. [14].

†Measurements at 320 nm were not possible due to the high absorbance at these high concentrations.

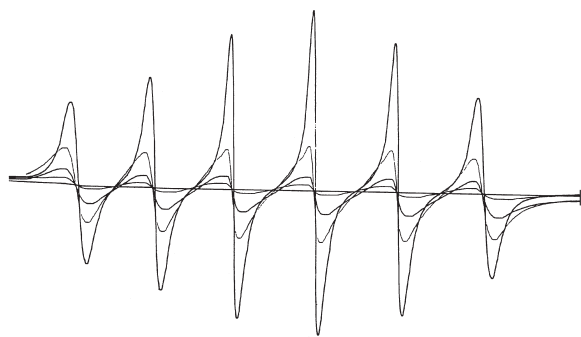


FIGURE 2 EPR titration of MnI_2 at 20°C in acetonitrile with stepwise addition of **1c** (0.2 equiv). Pure MnI_2 gives a sextet ($g = 2.0105$, $A_{\text{Mn}^{2+}} = 95.8$), with 0.8 equivalents of **1c** the peaks disappear completely.

caused by coupling phenomena in the unsymmetrical ligand field within the concave ligand. In contrast to the titration of MnI_2 with **1c**, for **1a**· MnI_2 a remaining signal of 5% of its original height was found, even when an excess of **1a** was added (1.4 equiv.). The observation of a remaining signal is in accordance with a lower association constants for **1a** in comparison to **1c**. At 1:1 stoichiometry with $[\text{Mn}^{2+}]_{\text{total}} = 2 \text{ mM}$ and $\log K_{\text{assoc}} = 4.7$, the concentration of free manganese ion concentration is calculated to be $[\text{Mn}^{2+}]_{\text{uncomplexed}} = 0.2 \text{ mM}$. Taken into account that signal height does not correlate linearly with concentration, that the EPR signal may be smaller due to kinetic processes on the same time scale, that ligand **1a** has been used in slight excess

TABLE IV E_{pa} , E_{pc} and $E_{1/2}$ values of the transition metal salts and their complexes with 1,10-phenanthrolines **1** and **2** against saturated calomel electrode (SCE), (solvent: acetonitrile[¶], $[\text{NBu}_4\text{PF}_6] = 100 \text{ mM}$, scan rate: 100 mV/s , internal standard: ferrocene ($E_{1/2} = 0.34 \text{ V}_{\text{SCE}}^{\S}$))

Metal salt/complex*	Potential
2	No signal
FeNf_2	$E_{\text{pc}} = -0.83 \text{ V}$, -1.43 V
2 · FeNf_2	$E_{1/2} = -1.27 \text{ V}$, -1.62 V
1c	$E_{\text{pa}} = +2.0 \text{ V}^{\dagger}$
CoNf_2	$E_{\text{pc}} = -0.95 \text{ V}$
1c · CoNf_2	$E_{1/2} = -0.87 \text{ V}$, $E_{\text{pc}} = -1.27 \text{ V}$
CoI_2^{\ddagger}	$E_{1/2} = 0.39, 0.19$, $E_{\text{pc}} = -0.66^{\S}$, -0.87 V^{\S}
1c · CoI_2^{\ddagger}	$E_{1/2} = 0.61, 0.21$, $E_{\text{pc}} = -0.79$, -1.55 V

*For irreversible experiments see footnote[¶]. [†]Shoulder on the solvent peak. [‡]Internal standard: Tris(*p*-bromophenyl)-amine: $E_{1/2} = 1.06 \text{ V}$ (SCE). [¶]Badly separated signals (electrode covering). [§]More complexes were measured the same way: **2**· HClO_4 : $E_{\text{pc}} = -0.84 \text{ V}$, $E_{\text{pa}} = 1.71 \text{ V}$, 2.03 V . **2**· CuBr_2 [‡]: broad irreproducible signals, no interpretation possible. MnNf_2 : $E_{\text{pc}} = -0.66 \text{ V}$, -1.42 V . **1c**· MnNf_2 : $E_{\text{pc}} = -1.48 \text{ V}$. MnI_2 [‡]: $E_{\text{pc}} = -1.61 \text{ V}$. **1c**· MnI_2 [‡]: $E_{1/2} = 0.58, 0.31$, $E_{\text{pc}} = -1.42 \text{ V}$. FeNf_2 : $E_{\text{pc}} = -0.83 \text{ V}$, -1.43 V . **1c**· FeNf_2 : $E_{\text{pc}} = -1.24 \text{ V}$. NiNf_2 : $E_{\text{pc}} = -0.99 \text{ V}$. **1c**· NiNf_2 : $E_{\text{pc}} = -0.97 \text{ V}$, -1.57 V . NiI_2 : $E_{\text{pc}} = -0.77$, -1.06 V . **1c**· NiI_2 : $E_{1/2} = 0.59, 0.18 \text{ V}$, $E_{\text{pc}} = -1.57$, -1.92 V . CuI : $E_{\text{pc}} = -0.12, 0.62, 0.95 \text{ V}$, $E_{\text{pa}} = 0.12, 0.26, 0.73, 1.05 \text{ V}$. **1c**· CuI : $E_{\text{pc}} = -0.26, 0.32, 0.89 \text{ V}$, $E_{\text{pa}} = 0.07, 0.10, 0.75, 0.97 \text{ V}$, $E_{1/2} = -1.36 \text{ V}$. [§]Internal standard: Tris(*p*-bromophenyl)-amine: $E_{1/2} = 1.06 \text{ V}$ (SCE). [¶]The $E_{1/2}$ value for ferrocene is not defined exactly vs. SCE. In this work $E_{1/2} = 0.34 \text{ V}_{\text{SCE}}$ was used. [¶]Acetonitrile was refluxed over powdered CaH_2 in an argon atmosphere and was distilled using a column.

and that both measurements have their errors, the data observed from the EPR experiments and from the UV titrations are in reasonable agreement. Using ligand **1c**, the EPR signal disappears completely (at 1:1 stoichiometry: $[\text{Mn}^{2+}]_{\text{total}} = 2 \text{ mM}$; $\log K_{\text{assoc}} \gg 7$; $[\text{Mn}^{2+}]_{\text{uncomplexed}} < 0.02 \text{ mM}$).

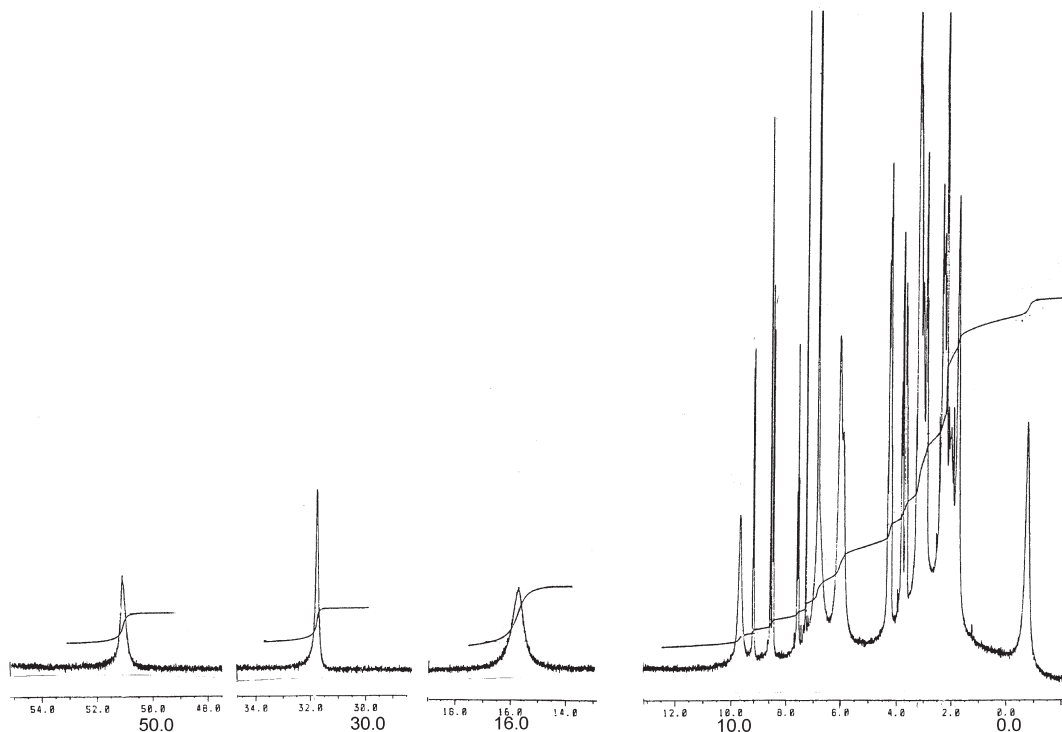


FIGURE 3 ^1H NMR spectrum of **1c**· FeNf_2 at 297 K in CDCl_3 .

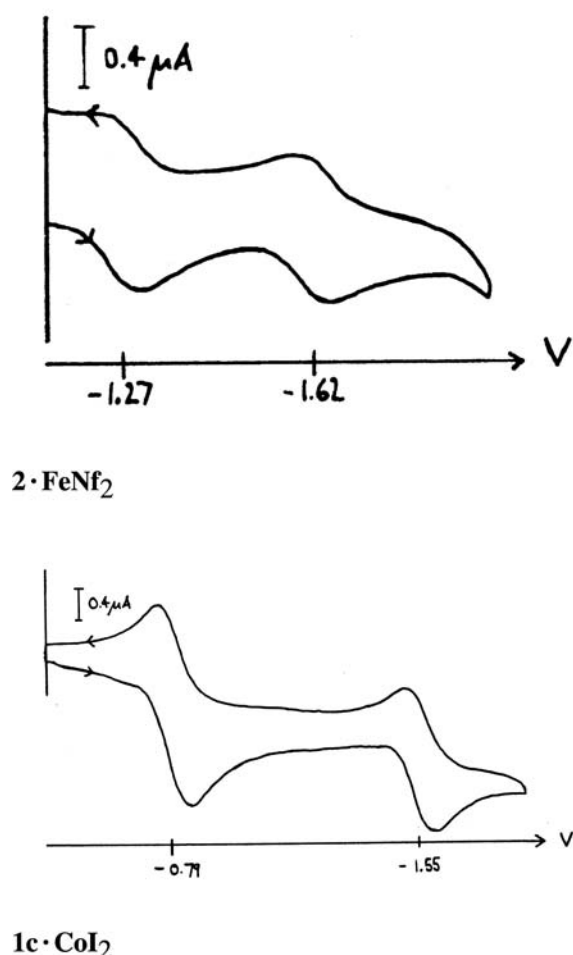


FIGURE 4 Cyclovoltammograms of $2 \cdot \text{FeNf}_2$ and $1\text{c} \cdot \text{CoI}_2$, scan rate 100 mV/s, [complex] = 1 mM, electrolyte: NBu_4PF_6 .

^1H NMR Measurements

Metal complexes with an even number of electrons can be investigated by NMR spectroscopy if all electrons are paired (low spin). Besides the Cu^+ complexes [13], Ni^{2+} , Fe^{2+} and Ag^+ complexes have been investigated by ^1H NMR. In analogy to the protonation of the bimakrocycles **1a–1c** [13,14], complexation of metal ions to **1c** or **2** led to lowfield shifts in the NMR spectra.

While $1\text{c} \cdot \text{NiNf}_2$ only gave broad paramagnetic signals like $1\text{c} \cdot \text{MnI}_2$, $1\text{c} \cdot \text{FeNf}_2$ showed a set of para- and diamagnetic peaks (ratio ca. 2:1, Fig. 3). The diamagnetic signals shifted up to 0.8 ppm in comparison to **1c**. Temperature variation from 212 to 331 K did not change the ratio of the paramagnetic and diamagnetic signals, but the paramagnetic resonances shifted considerably in a range of 70 ppm (selected signals see "Experimental Section").

According to previous investigations [13], shifts of the ligand protons in Cu^+ complexes depended on the complex geometry. In $2 \cdot \text{CuBr}$ (1:1 complex), shifts of the 1,10-phenanthroline hydrogen atoms of up to 0.2 ppm towards lower field were found. In contrast,

in $[2]_2 \cdot \text{CuNf}$ (2:1 complex) the CH_3 -hydrogen atoms appear 0.7 ppm at higher field. This finding is in agreement with a tetrahedral complexation of the copper ion by two 1,10-phenanthroline units. In such a 2:1 complex, the *ortho* methoxy groups are located in the anisotropic cone of the aromatic 1,10-phenanthroline system.

Cyclovoltammetry (CV)

Many metal ions can exist in at least two oxidation states. Therefore CV experiments for oxidation and reduction of some complexes were carried out in dry acetonitrile with a Pt working electrode and an Ag/Ag^+ reference electrode using tetrabutylammonium hexafluorophosphate (NBu_4PF_6) as electrolyte (see Table IV).

Cyclovoltammograms of the concave 1,10-phenanthroline **1c** between -1.5 V and $+2.5$ V showed an oxidation peak beyond $+2.0$ V which could not be separated from the solvent peak. For **2**, no CV signal was detectable.

For most complexes, the voltammograms did not show reversible electron transfers. In acetonitrile, the investigated pure metal salts always showed irreversible reduction waves caused by a two-electron transfer accompanied by electrode covering. For the iron and cobalt complexes $2 \cdot \text{FeNf}_2$, $1\text{c} \cdot \text{CoNf}_2$ and $1\text{c} \cdot \text{CoI}_2$ reversible CV peaks corresponding to the Co^0 to Co^+ and to Co^{2+} oxidation and to the Fe^0 to Fe^+ and to Fe^{2+} oxidation could be observed.[¶] Comparison with the pure metal salt and the pure ligand showed that the organic unit stabilizes the mono-charged oxidation state (Co^+ , Fe^+). Apparently complexation increases the electron density with the consequence that the reduction potential from M^+ to M^0 shifts to more negative values (Fig. 4).

The electrochemical investigation of the complex $1\text{c} \cdot \text{CuI}$ did not show reversible electron transfers for $\text{Cu}^+/\text{Cu}^{2+}$, but in separate experiments it was possible to isolate the copper bimakrocycle complex in both oxidation states.

INVESTIGATIONS IN THE SOLID STATE

Microanalyses

A number of complexes were isolated as solids and could be obtained in analytically pure quality as 1:1 complexes by recrystallization whereas other compounds refused to crystallize in a defined composition. For the open chain 1,10-phenanthroline **2** various complex stoichiometries have been found. **2** and $\text{Fe}(\text{ClO}_4)_2$ crystallize as a 2:1 compound, whereas FeNf_2 crystallizes with **2** in a 1.5:1 ratio [24]. FeCl_3 precipitated with **2** as a 1:1 complex. With CoI_2 and **2**, a 3:1, and with NiI_2 and **2**, a 2.6:1

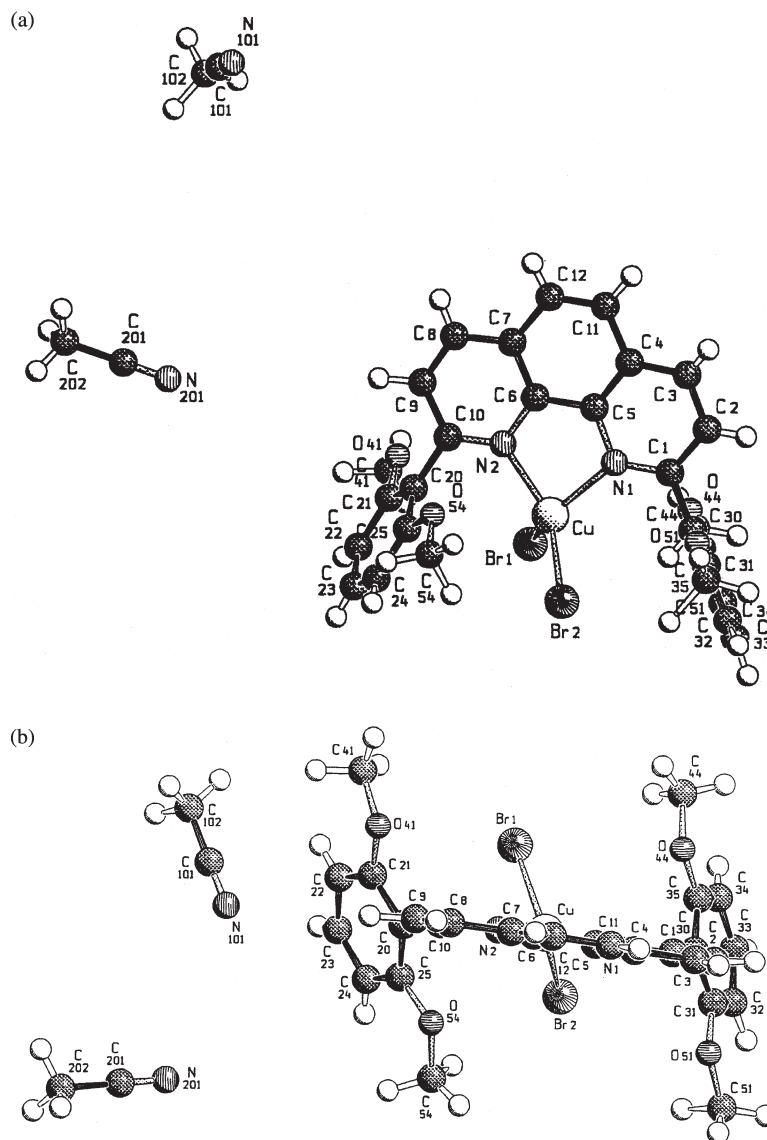


FIGURE 5 X-ray structure of 2-CuBr_2 , (a) view perpendicular to the 1,10-phenanthroline-plane, (b) view from above.

stoichiometry were found [24]. The CuBr and CuBr_2 complexes of **2** exist as 1:1 complexes whereas the copper(I) ion in the complex of CuNf with **2** is tetrahedrally coordinated by two ligands. For the concave 1,10-phenanthroline ligands **1**, 1:1 complex stoichiometries have been found. The 3:2 stoichiometry of **1a**· MnI_2 is an exception. Maybe the 1:1 complex and the free ligand crystallize as a mixture. In solution, the EPR and UV measurements argue for a 1:1 complex stoichiometry (see above).

X-ray Analysis

Unfortunately, complexes of the transition metal salts with concave 1,10-phenanthrolines **1** did not crystallize as single crystals. However the complex of the non-macrocyclic ligand **2** with CuBr_2 gave single crystals. The geometry of this complex has been confirmed by X-ray analysis (Fig. 5).

The X-ray structure of 2-CuBr_2 shows that the d^9 -copper(II) ion is coordinated almost tetrahedrally by the nitrogen donors of the 1,10-phenanthroline and by the bromide anions. The N–Cu–N (bond length 2.05 Å) and Br–Cu–Br (bond length 2.01 Å) planes enclose an angle of 65° , and the dihedral angle between the 1,10-phenanthroline system and the phenyl substituents enclose 69° and 75° . A comparison with X-ray analyses of two concave 1,10-phenanthrolines **1a** and **1b** [14], one with pure aliphatic, the other with polyether side chains, shows that the 1,10-phenanthroline phenyl distortion is not changed much by metal ion complexation. The similar structures of the rigid backbone of the 1,10-phenanthroline substituted by phenyl units in 2,9-positions in the bimakrocycles **1a** and **1b** and in 2-CuBr_2 allow two conclusions: concave ligands and concave complexes have comparable structures, and the metal ion interacts with the basic nitrogen

TABLE V xyz-Coordinates of the X-ray structure of 2-CuBr₂

Atom	x	y	z	B (Å ²)
Br1	0.89813	0.37540 (4)	0.15533 (3)	4.81 (10)
Br2	1.04659 (4)	0.07019 (4)	0.22169 (4)	5.29 (1)
Cu	0.98824 (4)	0.25074 (4)	0.29773 (4)	3.38 (1)
O41	0.6134 (3)	0.4975 (2)	0.3179 (2)	5.33 (7)
O44	1.2268 (3)	0.3777 (2)	0.1759 (2)	4.71 (7)
O51	1.3552 (3)	0.0088 (2)	0.3477 (2)	5.04 (7)
O54	0.7957 (3)	0.1143 (2)	0.4316 (2)	5.35 (7)
N1	1.1270 (2)	0.2638 (2)	0.3852 (2)	2.77 (6)
N2	0.8902 (2)	0.3203 (2)	0.4273 (2)	2.96 (6)
N101	0.3184 (8)	0.7084 (7)	1.1126 (6)	24.1 (3)
N201	0.2831 (4)	0.1633 (4)	0.7937 (3)	7.0 (1)
C1	1.2442 (3)	0.2376 (3)	0.3615 (3)	3.00 (7)
C2	1.3252 (3)	0.2546 (3)	0.4339 (3)	3.73 (8)
C3	1.2837 (3)	0.3044 (3)	0.5280 (3)	3.80 (8)
C4	1.1611 (3)	0.3367 (3)	0.5537 (3)	3.23 (8)
C5	1.0852 (3)	0.3143 (3)	0.4808 (2)	2.86 (7)
C6	0.9592 (3)	0.3455 (3)	0.5023 (2)	2.90 (7)
C7	0.9105 (3)	0.3996 (3)	0.5969 (3)	3.25 (8)
C8	0.7860 (4)	0.4264(3)	0.6126 (3)	3.94 (9)
C9	0.7175 (3)	0.3991 (3)	0.5392 (3)	3.90 (9)
C10	0.7726 (30)	0.3432 (3)	0.4465 (3)	3.22 (7)
C11	1.1088 (3)	0.3949 (3)	0.6486 (3)	3.64 (8)
C12	0.9904 (4)	0.4245 (3)	0.6682 (3)	3.65 (8)
C20	0.7019 (3)	0.3032 (3)	0.3706 (3)	3.63 (8)
C21	0.6231 (3)	0.3808 (4)	0.3051 (3)	4.26 (9)
C22	0.5611 (4)	0.3397 (4)	0.2327 (3)	5.4 (1)
C23	0.5800 (4)	0.2207 (4)	0.2266 (4)	6.2 (1)
C24	0.6551 (4)	0.1409 (4)	0.2903 (4)	5.6 (1)
C25	0.7175 (30)	0.1821 (3)	0.3629 (3)	4.39 (9)
C30	1.2889 (3)	0.1901 (3)	0.2560 (3)	3.12 (7)
C31	1.3459 (3)	0.0723 (3)	0.2504 (3)	3.63 (8)
C32	1.3879 (3)	0.0258 (3)	0.1527 (3)	4.27 (9)
C33	1.3728 (3)	0.1002 (4)	0.0613 (3)	4.41 (9)
C34	1.3199 (4)	0.2155 (4)	0.0645 (3)	4.33 (9)
C35	1.2775 (3)	0.2620 (3)	0.1623 (3)	3.57 (8)
C41	0.5632 (5)	0.5787 (5)	0.2339 (4)	7.1 (1)
C44	1.2067 (5)	0.4550 (4)	0.0811 (4)	6.9 (1)
C51	1.4037 (6)	-0.1142 (4)	0.3449 (4)	8.2 (2)
C54	0.8197 (5)	-0.0106 (4)	0.4276 (4)	7.2 (1)
C101	0.2688 (6)	0.7790 (6)	1.0601 (5)	11.3 (2)
C102	0.2093 (5)	0.8654 (5)	0.9919 (4)	7.6 (2)
C201	0.1940 (4)	0.1762 (4)	0.8367 (3)	5.8 (1)
C202	0.0784 (6)	0.1918 (6)	0.8928 (5)	9.5 (2)
H2	1.405 (30)	0.243 (3)	0.412 (2)	3.9 (8)*
H3	1.330 (3)	0.313 (3)	0.572 (3)	4.8 (9)*
H8	0.755 (3)	0.462 (3)	0.676 (3)	6 (1)*
H9	0.625 (3)	0.413 (3)	0.554 (2)	4.1 (8)*
H11	1.165 (3)	0.410 (3)	0.696 (3)	5.2 (9)*
H12	0.953 (3)	0.461 (3)	0.725 (3)	5.5 (9)*
H22	0.512 (3)	0.388 (3)	0.183 (3)	6 (1)*
H23	0.542 (3)	0.204 (3)	0.176 (3)	7 (1)*
H24	0.666 (3)	0.064 (3)	0.289 (2)	3.8 (8)*
H32	1.430 (3)	-0.059 (3)	0.150 (3)	6 (1)*
H33	1.399 (3)	0.066 (3)	-0.005 (2)	3.9 (8)*
H34	1.309 (3)	0.257 (3)	0.006 (2)	4.1 (8)*
H41c	0.571 (4)	0.656 (4)	0.243 (3)	10 (1)*
H41a	0.594 (4)	0.559 (4)	0.169 (3)	9 (1)*
H41n	0.470 (4)	0.583 (4)	0.242 (3)	8 (1)*
H44a	1.286 (3)	0.459 (3)	0.047 (3)	6 (1)*
H44b	1.151 (4)	0.434 (3)	0.040 (3)	7 (1)*
H44c	1.156 (4)	0.528 (4)	0.107 (3)	8 (1)*
H51a	1.404 (3)	-0.136 (3)	0.411 (3)	6 (1)*
H51b	1.493 (4)	-0.142 (4)	0.321 (3)	9 (1)*
H51c	1.329 (8)	-0.147 (7)	0.285 (7)	26 (4)*
H54c	0.738 (4)	-0.032 (4)	0.440 (4)	11 (2)*
H54a	0.858 (5)	-0.025 (4)	0.340 (4)	12 (2)*
H54b	0.884 (4)	-0.050 (4)	0.468 (4)	10 (1)*
H100	0.147	0.831	0.946	4.0**
H101	0.260	0.903	0.940	9.7**
H102	0.160	0.933	1.031	9.7**
H200	0.083	0.187	0.970	4.0**
H201	0.033	0.134	0.876	12.2**
H202	0.024	0.268	0.872	12.2**

*Isotropic refinement.

**Not refined.

atoms of the bimacrocycles **1** in the cavity in the same way as in 2·CuBr₂. The search for suitable single crystals of metal complexes of the concave 1,10-phenanthrolines **1** is on going (Table V).

CONCLUSION

Concave 1,10-phenanthrolines **1** are good ligands for the complexation of transition metal ions. The complex formation can be analyzed qualitatively and quantitatively by a variety of analytical methods. Due to their special geometry, they exclusively form 1:1 complexes with transition metal ions leaving some coordination sites of the metal ion open for the coordination of further, smaller ligands. This is a prerequisite for catalytic activity which has already been shown for some complexes [18–22]. In these catalytic reactions, the concave shielding of the catalytic center by the concave ligand leads to remarkable selectivities.

EXPERIMENTAL

The organic ligands **1** and **2** and the transition metal nonafluorobutanesulfonates MnF_n were synthesized as described [13,14]. For solvent preparation and general equipment see [13].

EPR measurements: BER 420, Fa. Bruker. All spectra were measured in acetonitrile at room temperature: MnI₂ and titration of MnI₂ with **1a** and **1c** ($\nu = 9.641$ GHz, center field: 3500 G, modulation 16 G, time constant 0.5 s, sweep time 200 s, sweep wide 1000 G, enhancement 2.5×10^4 , microwave power 4 mW): $g = 2.0105$, $A_{\text{Mn}^{2+}} = 95.8$ G. CoI₂ ($\nu = 9.639$ GHz, center field: 3600 G, modulation 16 G, time constant 0.2 s, sweep time 200 s, sweep wide 1000 G, enhancement 1.25×10^6 , microwave power 4 mW): $g = 2.1054$, $A_{\text{Co}^{2+}} = 94.6$ G. NiI₂ (in CH₃CN/H₂O) ($\nu = 9.643$ GHz, center field: 3000 G, modulation 20 G, time constant 0.2 s, sweep time 200 s, sweep wide 2500 G, enhancement 2×10^5 , microwave power 4 mW): $g = 2.009$, $A_{\text{Ni}^{2+}} = 96.1$ G. No EPR signals were observed for **1a**, **1c**, **1a**·MnI₂, **1c**·MnI₂, **1c**·CoI₂, **1c**·NiI₂.

CV measurements: Scanning potentiostat 326, Fa. Princeton. XYt recorder PM 8271 Fa. Philips, Pt working electrode, Ag/Ag⁺ reference electrode, NBu₄PF₆ as electrolyte in dry acetonitrile.

SYNTHESES OF THE TRANSITION METAL COMPLEXES

General procedures: Only complexes with satisfactory microanalyses are described.

Method A: A solution of the transition metal salt in 5–20 ml of dry methanol was added slowly to a

solution of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**) in 5–20 ml of dry dichloromethane. After stirring for 2 h at room temperature, the solvents were distilled off *in vacuo* and the solid residue was recrystallized.

Method B: Stoichiometric amounts (40–80 mmol) of the concave 1,10-phenanthroline **1** and the transition metal salt were dissolved in 50–80 ml of dry acetonitrile and the mixture was stirred at room temperature for 1 h. The solvent was distilled off and the solid residue was recrystallized.

Method C: The concave 1,10-phenanthroline **1** was dissolved in 5–10 ml of dry dichloromethane. The dry metal salt in 5–10 ml of dry methanol was added over 2 h at room temperature while stirring. After evaporation, the solid residue was recrystallized.

Mn²⁺ Complexes

6,15,33,42-Tetraoxa-43,46-diazaheptacyclo-[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]-hexatetraconta-1(32),2,4,16,18,20,22,24,26,28,30,43,45-tridecaene Manganese(II) Iodide (1a·MnI₂)

According to method C, 49 mg (0.16 mmol) of dry MnI₂ was added to 100 mg (0.16 mmol) of **1a**. After recrystallization from petroleum ether (b p: 60–70°C)/acetone a light yellow solid was obtained (119 mg, 89%), mp > 330°C; [C₄₀H₄₄N₂O₄]₃[MnI₂]₂ (2466.68): Calcd: C 58.40, H 5.39, N 3.40, Found: C 58.01, H 5.32, N 3.33; IR (KBr): ($\bar{\nu}$) cm⁻¹ 2905, 2830 (CH₃), 1600, 1460 (arom.), 1250, 1100 (C–O–C).

6,9,12,15,33,36,39,42-Octaoxa-43,46-diazaheptacyclo-[18.12.10.4^{22,31}.0^{5,32}.0^{16,21}.0^{25,45}.0^{28,44}]-hexatetraconta-1(32),2,4,16,18,20,22,24,26,28,30,43,45-tridecaene Manganese(II) Nonafluorobutanesulfonate (1b·MnNf₂)

According to method B, 100.5 mg (153.8 μmol) of MnNf₂ was added to 96.1 mg (153.8 μmol) of **1b**. After recrystallization from water/methanol, 149 mg (71%) of a slightly yellow solid was obtained, mp > 250°C; C₄₄H₃₆F₁₈MnN₂O₁₄S₂ (1277.80) Calcd. C 41.36, H 2.84, N 2.19, Found C 41.61, H 3.25, N 2.31; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1603, 1472, 1454 (arom.), 1265, 1056 (C–O–C), 1255, 1220 (SO₂), 868, 736, 656 (arom.).

6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Manganese(II) Iodide (1c·MnI₂)

According to method C, 12 mg (0.04 mmol) of dry MnI₂ was added to 30 mg (0.04 mmol) of **1c** and the light yellow solid was recrystallized from benzene/acetonitrile (37.2 mg, 91%), mp > 250°C; C₄₀H₄₄I₂MnN₂O₁₀ (1021.52) Calcd C 47.03, H 4.34, N 2.74, Found C 46.85, H 4.21, N 2.67; IR (KBr): ($\tilde{\nu}$) cm⁻¹ 1600, 1470 (arom.), 1255, 1095 (C–O–C); ¹H NMR (250 MHz, CDCl₃) δ = 1.0, 2.0, 3.5 (very broad peaks caused by paramagnetic Mn²⁺).

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Manganese(II) Iodide (2·MnI₂)

According to method A, 205 mg (660 μ mol) of dry MnI₂ was added to 300 mg (660 μ mol) of **2**. The resulting yellow solid was recrystallized from methanol/acetonitrile, yielding 2·MnI₂ (405 mg, 81%), mp > 330°C; C₂₈H₂₄MnI₂N₂O₄ (761.02): Calcd: C 44.2, H 3.2, N 3.75, Found: C 44.6, H 3.3, N 4.4; IR (KBr): ($\tilde{\nu}$) cm⁻¹ 1590, 1465 (arom.), 1250, 1100 (C–O–C).

Fe²⁺ Complexes

6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Iron(II) Nonafluorobutanesulfonate (1c·FeNf₂)

According to method B, 50.0 mg (76.4 μ mol) of iron(II)nonafluorobutanesulfonate was added to 57.2 mg (76.4 μ mol) of **1c**. The yellow residue was recrystallized from water/methanol (67.8 mg, 65%), mp 114°C; C₄₈H₄₄F₁₈FeN₂O₁₆S₂ (1366.45): Calcd: C 42.18, H 3.25, N 2.05, Found: C 42.85, H 3.66, N 2.10. ¹H NMR (400 MHz, CDCl₃, 30°C): δ = -0.65 (br. s, para.), 1.80 (br. s, para.), 2.10 (br. s, para.), 2.30 (br. s, para.), 2.95 (*m_c*, 4 H, CH₂), 3.0 (br. s, para.), 3.15 (*m_c*, 4 H, CH₂), 3.29 (*m_c*, 8 H, CH₂), 3.63 (*m_c*, 4 H, CH₂), 3.78 (*m_c*, 4 H, CH₂), 4.29 (*m_c*, 4 H, CH₂), 4.37 (*m_c*, 4 H, CH₂), 6.54 (br. *m_c*, para.), 6.85 (d, *J* = 9 Hz, ca. 4 H, H_{3/5}), 7.55 (t, *J* = 9 Hz, ca. 2 H, H₄), 8.45 (d, *J* = 9 Hz, ca. 2 H, H_{3/8}), 8.54 (s, 2 H, H_{5/6}), 9.16 (d, *J* = 9 Hz, ca. 2 H, H_{4/7}), 9.72 (br. s, para.), 15.30 (br. s, para.), 31.25 (br. s, para.), 48.85 (br. s, para.); δ_{H} (400 MHz, CDCl₃, 59°C) -0.23 (br. s, para.), 1.68 (br. s, para.), 2.10 (br. s, para.), 2.60 (br. s, para.), 2.88 (*m_c*, 4 H, CH₂), 3.10 (*m_c*, 4 H, CH₂), 3.16 (*m_c*, 8 H, CH₂), 3.62 (*m_c*, 4 H, CH₂), 3.72 (*m_c*, 4 H, CH₂), 4.20 (*m_c*, 4 H, CH₂), 4.28 (*m_c*, 4 H, CH₂), 5.22 (br. s, para.), 5.55 (br. s, para.), 6.86 (d, *J* = 9 Hz, ca. 4 H, H_{3/5}), 7.57 (t, *J* = 9 Hz, ca. 2 H, H₄), 8.43 (s, 2 H, H_{5/6}), 8.47 (d, *J* = 9 Hz, ca. 2 H,

phen), 9.10 (d, *J* = 9 Hz, ca. 2 H, phen), 9.60 (br. s, para.), 14.55 (br. s, para.), 28.80 (br. s, para.), 45.80 (br. s, para.); ¹H NMR (400 MHz, CDCl₃, -61°C): δ = -5.8 (br. s, para.), -1.0 (br. s, para.), 0.3 (br. s, para.), 2.8 (*m_c*, 6 H, CH₂), 3.4 (*m_c*, 10 H, CH₂), 3.7 (*m_c*, 4 H, CH₂), 3.8 (*m_c*, 4 H, CH₂), 4.3 (*m_c*, 8 H, CH₂), 6.9 (s, 4 H, H_{3/5}), 7.6 (s, 2 H, H₄), 8.3 (s, 2 H, phen), 8.8 (s, 2 H, phen), 9.3 (s, 2 H, phen), 22.5 (br. s, para.), 44.0 (br. s, para.), 70.2 (br. s, para.); ¹H NMR (250 MHz, [D₆]-DMSO, 25°C): δ = 2.81 (*m_c*, 8 H, CH₂), 3.30 (*m_c*, 4 H, CH₂), 3.54 (*m_c*, 4 H, CH₂), 3.92 (*m_c*, 16 H, CH₂), 6.71 (d, *J* = 9 Hz, 4 H, H_{3/5}), 7.57 (t, *J* = 9 Hz, 2 H, H₄), 7.63 (br. s, 2 H, H_{3/8}), 8.03 (br. s, 2 H, H_{5/6}), 8.48 (br. s, 2 H, H_{4/7}); ¹³C NMR (100 MHz, CDCl₃): δ = 69.26, 69.65, 70.01, 70.29, 70.34, 70.73, 70.81, 106.45, 127.62, 128.21, 129.63, 131.38, 133.60, 135.48, 141.03, 153.09, 157.39. *: para. = very broad signals caused by paramagnetic Fe²⁺.

Bis[2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline] Iron(II) Perchlorate ([2]₂·Fe(ClO₄)₂)

According to method A, 0.642 g (1.76 mmol) of Fe(ClO₄)₂·6 H₂O was added to 0.80 g (1.76 mmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**). The solvents were distilled off (an analytical sample was dried and was shown to be stable against shock and heating) and the yellow precipitate was recrystallized from dichloromethane/methanol as yellow needles (0.72 g, 71%), mp > 250°C (dec.); C₅₆H₄₈Cl₂FeN₄O₁₆ (1159.80): Calcd: C 58.00, H 4.17, N 4.83, Found: C 58.18, H 4.20, N 4.61; IR (KBr): ($\tilde{\nu}$) cm⁻¹ 3000, 2925, 2825 (CH₃), 1595, 1470 (arom.), 1255, 1245, 1110, 1085 (C–O–C); ¹H NMR (250 MHz, CDCl₃): δ = 3.83 (s, 12 H, CH₃), 6.88 (d, *J* = 8 Hz, 4 H, H_{2/6}), 7.58 (t, *J* = 8 Hz, 2 H, H₄), 8.23 (s, 2 H, H_{5/6}), 8.35 (d, *J* = 8 Hz, 2 H, H_{3/8}), 8.85 (d, *J* = 8 Hz, 2 H, H_{4/7}). Remark: The ¹H NMR spectrum showed additional broad peaks between 1.0–1.2 ppm and 3.2–3.7 ppm.

Fe³⁺ Complex

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Iron(III) Chloride (2·FeCl₃)

According to method A, 282 mg (1.74 mmol) of dry FeCl₃ was added to 785 mg (1.74 mmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**) (dried over active molecular sieve (4 Å) in solution). The solvents were distilled off and the brown air stable residue was recrystallized from dichloromethane/acetonitrile (336 mg, 31 %), mp: 228–230°C; C₂₈H₂₄Cl₃FeN₂O₄·0.5 H₂O (614.49 + 9.00): Calcd: C 53.92, H 4.04, N 4.49, Found: C 53.76, H 4.05, N 4.49; IR (KBr): ($\tilde{\nu}$) cm⁻¹ 1595, 1473 (arom.), 1250, 1104, 1018 (C–O–C).

Co²⁺ Complexes**6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Cobalt(II) Nonafluorobutanesulfonate (1c-CoNf₂)**

According to method B, 32.5 g (49.5 mmol) of CoNf₂·3 H₂O was added to 37.1 mg (49.5 mmol) of **1c**. The solid was recrystallized from dioxane to give a white solid (15.1 mg, 22%), mp 136°C; C₄₈H₄₄CoF₁₈N₂O₁₆S₂·5 H₂O (1369.94 + 90.10): Calcd: C 39.49, H 3.73, N 1.92, Found: C 39.53, H 3.42, N 2.03; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1590, 1460 (arom.), 1345, 1200 (C–F), 1280, 1085 (C–O–C), 1240, 1050 (SO₂).

6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Cobalt(II) Iodide (1c-CoI₂)

According to method B, 13 mg (0.04 mmol) of dry CoI₂ was added to 30 mg (40 μmol) of **1c** and the green solid was recrystallized from toluene/acetonitrile to a light green solid (16 mg, 37%), mp > 250°C; C₄₀H₄₄CoI₂N₂O₁₀·4 H₂O (1097.51 + 72.04): Calcd: C 43.77, H 4.76, N 2.55, Found: C 43.84, H 4.83, N 2.31; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1600, 1460 (arom.), 1250, 1100 (C–O–C).

Tris[2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline] Cobalt(II) Iodide ([I]₃CoI₂)

According to method A, 141 mg (0.55 mmol) of dry CoI₂ was added to 408 mg (1.10 mmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**). The resulting orange solid was recrystallized from toluene/acetonitrile (146 mg, 24%), mp 245°C; C₈₄H₇₂CoI₂N₆O₁₂ (1669.57): Calcd: C 60.41, H 4.35, N 5.03, Found: C 60.18, H 4.10, N 5.05; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1595, 1465 (arom.), 1245, 1110 (C–O–C).

Ni²⁺ Complex**6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Nickel(II) Nonafluorobutanesulfonate (1c-NiNf₂)**

According to method B, 57 mg (81 μmol) of NiNf₂·4 H₂O was added to 61 mg (81 μmol) of **1c**. The solid was recrystallized from water/methanol to give green crystals (89 mg, 80%), mp 86°C; C₄₈H₄₄F₁₈N₂NiO₁₆S₂·4 H₂O (1441.41): Calcd: C 39.99, H 3.64, N 1.94, Found: C 39.80, H 3.42, N 1.88; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1590, 1460 (arom.), 1345, 1210 (C–F), 1280, 1085

(C–O–C), 1240, 1050 (SO₂); ¹H NMR (250 MHz, CDCl₃): δ = 2.6–3.6 (2 peaks), 3.5–4.1, 5.3 (s), 5.1–6.1, 8.6–9.2, 11.6–12.2, 12.6–14.6, 17.1–17.5, 22.4. Remark: Very broad signals caused by paramagnetic Ni²⁺.

Cu⁺ Complexes**2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Copper(I) Bromide (2-CuBr)**

According to method A, 195 mg (660 μmol) of dry CuBr was added as solid under nitrogen to 300 mg (660 μmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**). The resulting dark red solution was evaporated and the residue recrystallized from methanol (301 mg, 77%), mp > 330°C; C₂₈H₂₄BrCuN₂O₄·0.75 H₂O (609.47): Calcd: C 55.18, H 4.21, N 4.60, Found: C 55.15, H 4.11, N 4.34; IR (KBr): ($\bar{\nu}$) cm⁻¹ 1595, 1465 (arom.), 1240, 1100 (C–O–C); ¹H NMR (250 MHz, CDCl₃): δ = 1.5 (s, >1 H₂O), 3.76 (s, 12 H, CH₃), 6.70 (d, J = 8 Hz, 4 H, H₄), 7.42 (t, J = 8 Hz, 2 H, H_{3/5}), 7.85 (d, J = 8 Hz, 2 H, H_{3/8}), 7.92 (s, 2 H, H_{5/6}), 8.38 (d, J = 8 Hz, 2 H, H_{4/7}).

Bis[2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline] Copper(I) Nonafluorobutanesulfonate ([I]₂-CuNf)

According to method A, but under nitrogen, 1.7 g (4 mmol) of acetonitrilo-copper(I) nonafluorobutanesulfonate was added to 3.5 g (8.0 mmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**). The residue was recrystallized from acetone to give red air stable crystals (4.50 g, 87%), mp 317–324°C; C₆₀H₄₈CuF₉N₄O₈ (1283.69): Calcd: C 56.85, H 3.82, N 4.42, Found: C 57.41, H 3.88, N 4.36; IR (KBr): ($\bar{\nu}$) cm⁻¹ 3480 (H₂O), 2905, 2810 (CH₃), 1595, 1465 (arom.), 1245, 1110 (C–O–C); ¹H NMR (250 MHz, CDCl₃): δ = 3.03 (s, 12 H, CH₃), 5.88 (d, J = 8 Hz, 4 H, H_{3/5}), 6.80 (t, J = 8 Hz, 2 H, H₄), 7.45 (d, J = 8 Hz, 2 H, H_{3/8}), 7.92 (s, 2 H, H_{5/6}), 8.26 (d, J = 8 Hz, 2 H, H_{4/7}); ¹³C NMR (100 MHz, CDCl₃): 54.37, 102.67, 115.65, 126.58, 127.66, 128.91, 130.26, 135.24, 144.58, 154.08, 157.07; ¹⁹F NMR (200 MHz, CFCl₃): δ = -81.37 (td, J_t = 12 Hz, J_d = 2 Hz, 3 F, CF₃), -114.90 (td, J_t = 12 Hz, J_d = 2 Hz, 2 F, CF₂), -121.89 (m_c, 2 F, CF₂), -126.31 (m_c, 2 F, CF₂).

Cu²⁺ Complexes**6,9,12,15,18,24,27,30,33,36-Decaoxa-49,52-diazaheptacyclo-[17.17.12.4^{38,47}.0^{5,37}.0^{19,48}.0^{41,50}.0^{44,51}]-dopentacont-1(37),2,4,19(48),20,22,38,40,42,44,46,49,51-tridecaene Copper(II) Bromide (1c-CuBr₂)**

According to method B, 23 mg (100 μmol) of dry CuBr₂ was added to a solution of 76 mg (100 μmol) of

1c in dry dichloromethane. After stirring at room temperature for 10 min the yellow solution changed color into a dark brown. After evaporation the dark brown solid was recrystallized from dichloromethane/methanol (32 mg, 34%), mp 210–212°C; $C_{40}H_{44}Br_2CuN_2O_{10} \cdot 1.5 H_2O$ (963.20): Calcd: C 49.88, H 4.92, N 2.91, Found: C 49.67, H 4.43, N 2.99; IR (KBr): ($\tilde{\nu}$) cm^{-1} 3400 (H_2O), 2900, 2845 (CH_3), 1590, 1460 (arom.), 1245, 1100 (C–O–C).

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Copper(II) Bromide (2·CuBr₂)

According to method A, 0.64 g (2.9 mmol) of CuBr₂ was added to 1.30 g (2.9 mmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**). The residue was recrystallized from benzene/acetonitrile to give dark red crystals (0.43 g, 22%), mp 180°C; $C_{28}H_{24}Br_2CuN_2O_4 \cdot 2 CH_3CN$ (757.67): Calcd: C 50.71, H 3.99, N 7.39, Found: C 50.62, H 3.97, N 7.07; IR (KBr): ($\tilde{\nu}$) cm^{-1} 2220 (CN), 1595, 1465 (arom.), 1245, 1120 (C–O–C); MS (CI, isobutane): m/z (%) = 676 ($M^+ + 1$, <0.5), 596 ($M^+ + 1 - Br$, 48), 516 ($M^+ + 1 - 2 Br$, 18), 453 ($M^+ + 1 - CuBr_2$).

X-ray data of 2·CuBr₂: Experimental parameters: Empirical formula: $C_{28}H_{24}N_2O_4 \cdot C_4H_6N_2$, molecular weight: 757.98, room temperature, wave length: 1.54184 Å, crystal system: triclinic, space group (P1bar) No. 2, $a = 1153(4)$ pm, $b = 1177(8)$ pm, $c = 1251(5)$ pm, $\alpha = 85.297(8)^\circ$, $\beta = 85.437(8)^\circ$, $\gamma = 76.159(9)^\circ$, $V = 1642.1(3) \times 10^6$ pm³, $Z = 2$, density_{calcd} = 1.533 g cm⁻³. Enraf Nonius CAD4 diffractometer, Cu–K α radiation, graphite monochromator, crystal size [mm]: 0.74 × 0.5 × 0.3, $\sin \theta / \lambda_{max} = 0.561$, reflections used for cell parameters: $28.4 < 2\theta < 44.0$, total no. of reflections: 5097, no. of independent reflections: 4849, no. of observed reflections ($I > 2\sigma(I)$): 4627, F(000): 762, absorption correction: max: 99.75, min: 49.19, absorption coefficient: $\mu = 41.345$ cm⁻¹, method of solution: direct (SIR 88), method of refinement: LSFM, parameters: 485, R , R_w : 0.040, 0.043, extinction coefficient: 0.000002074, program used: MOLEN (Enraf-Nonius, 1990).

Zn²⁺ Complex

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Zink Trifluoroacetate (2·Zn(OOCCF₃)₂)

A solution of zink trifluoroacetate (excess, the exact amount was unknown due to extreme hygroscopicity) in 3 ml of dry methanol was slowly added to 100 mg (220 μmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**) in 5 ml of dry dichloromethane. The mixture turned turbid, and after 2 h of stirring the solid was isolated by centrifugation. The white powder was washed with warm dichloro-

methane and warm acetone and was dried *in vacuo* yielding 117 mg (70%), mp > 250°C; $C_{32}H_{24}F_6N_2O_8 \cdot Zn \cdot H_2O$ (761.95): Calcd: C 50.45, H 3.44, N 3.68, Found: C 50.57, H 3.27, N 3.78; IR (KBr): ($\tilde{\nu}$) cm^{-1} 1703 (CO_2^-), 1599, 1476 (arom. C–H), 1255 (C–O–C), 1184 (C–F), 1111 (C–O–C).

Ag⁺ Complex

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Silver Trifluoroacetate (2·AgOOCCF₃)

A solution of 49.0 mg (220 μmol) of silver trifluoroacetate in 2 ml of dry methanol was added slowly to a solution of 100 mg (220 μmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**) in 5 ml of dry dichloromethane. After stirring for 2 h, the solvents were evaporated. The remaining solid was recrystallized from acetone/dichloromethane (5:1) yielding 123 mg (82%), mp > 250°C; $C_{30}H_{24}AgF_3N_2O_6 \cdot 0.5 H_2O$ (682.42): Calcd: C 52.80, H 3.69, N 4.11, Found: C 52.63, H 3.54, N 4.07; IR (KBr): ($\tilde{\nu}$) cm^{-1} 1677 (CO_2^-), 1598, 1472 (arom. C–H), 1250 (C–O–C), 1202 (C–F), 1106 (C–O–C); ¹H NMR (90 MHz, CDCl₃): $\delta = 3.75$ (s, 12 H, O–CH₃), 6.70 (d, $J = 9.0$ Hz, 4 H, H_{3'/5'}), 7.40 (t, $J = 9.0$ Hz, 2 H, H₄) 7.95 (d, $J = 9.0$ Hz, 2 H, H_{3/8}), 7.95 (s, 2 H, H_{5/6}), 8.45 (d, $J = 9.0$ Hz, 2 H, H_{4/7}).

Cd²⁺ Complex

2,9-Bis(2,6-dimethoxyphenyl)-1,10-phenanthroline Cadmium Trifluoroacetate [2·Cd(OOCCF₃)₂]

A solution of cadmium trifluoroacetate (excess, the exact amount was unknown due to a high water content) in 3 ml of dry methanol was added to a solution of 100 mg (220 μmol) of 2,9-bis(2,6-dimethoxyphenyl)-1,10-phenanthroline (**2**) in 5 ml of dry dichloromethane. After 2 h of stirring the solvents were evaporated, and the remaining residue was recrystallized from acetone/dichloromethane (1:3) yielding 133 mg (76%), mp > 250°C; $C_{32}H_{24}CdF_6N_2O_8 \cdot 0.5 H_2O$ (799.98): Calcd: C 48.05, H 3.16, N 3.50, Found: C 48.15, H 3.02, N 3.57; IR (KBr): ($\tilde{\nu}$) cm^{-1} 1676 (CO_2^-), 1588, 1475 (arom. C–H), 1251 (C–O–C), 1192 (C–F), 1104 (C–O–C).

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References

- [1] Schilt, A.A. (1969) Analytical Applications of 1,10-Phenanthroline and Related Compounds (Pergamon Press, Oxford).

- [2] Sammes, P.G. and Yahioğlu, G. (1994), *Chem. Soc. Rev.* **23**, 327–334.
- [3] Togni, A. and Venanzi, L.M. (1994), *Angew. Chem.* **106**, 517–547.
- [4] Togni, A. and Venanzi, L.M., (1994) *Angew. Chem., Int. Ed. Engl.* **33**, 497.
- [5] For overview: Wilkinson, G. (Ed.) (1987) *Comprehensive Coordination Chemistry* (Pergamon Press, Oxford).
- [6] For overview: *Gmelins Handbuch der anorganischen Chemie*, 8 Ed., VCH, Weinheim, for Ni²⁺: **57 C1** (1968) pp. 418–423, for Co²⁺: **58 B Erg. 1** (1963) pp. 100–105, for Cu⁺/2⁺: **60 B4** (1966) pp. 1525–1530.
- [7] Sauvage, J.-P. (1990), *Acc. Chem. Res.* **23**, 319–327.
- [8] Bitsch, F., Dietrich-Buchecker, C.O., Khémis, A.-K., Sauvage, J.-P. and Van Dorsselaer, A. (1991), *J. Am. Chem. Soc.* **113**, 4023–4025.
- [9] Dietrich-Buchecker, C.O., Guilhem, J., Pascard, C. and Sauvage, J.-P. (1990), *Angew. Chem.* **102**, 1202–1204.
- [10] C.O. Dietrich-Buchecker, J. Guilhem, C. Pascard and J.-P. Sauvage, (1990) *Angew. Chem., Int. Ed. Engl.* **29**, 1154.
- [11] Dietrich-Buchecker, C.O., Nierengarten, J.-F., Sauvage, J.-P., Armaroli, N., Balzani, V. and De Cola, L. (1993), *J. Am. Chem. Soc.* **115**, 11237–11244.
- [12] Ibukuro, F., Fujita, M., Yamaguchi, K. and Sauvage, J.-P. (1999), *J. Am. Chem. Soc.* **121**, 11014–11015.
- [13] Lüning, U. and Müller, M. (1990), *Chem. Ber.* **123**, 643–645.
- [14] Lüning, U., Müller, M., Gelbert, M., Peters, K., von Schnering, H.G. and Keller, M. (1994), *Chem. Ber.* **127**, 2297–2306.
- [15] Lüning, U. (1987), *Liebigs Ann. Chem.*, 949–955.
- [16] Lüning, U. (1995), *Top. Curr. Chem.* **175**, 57–99.
- [17] Lüning, U. (1997), *J. Mater. Chem.* **7**, 175–182.
- [18] Hagen, M. and Lüning, U. (1997), *Chem. Ber./Recueil* **130**, 231–234.
- [19] Löffler, F., Hagen, M. and Lüning, U. (1999), *Synlett*, 1826–1828.
- [20] Bühl, M., Terstegen, F., Löffler, F., Meynhardt, B., Kierse, S., Müller, M., Näther, C. and Lüning, U. (2001), *Eur. J. Org. Chem.*, 2151–2160.
- [21] Gelbert, M. and Lüning, U. (2001), *Supramolecular Chem.* **12**, 435–444.
- [22] Meynhardt, B., Lüning, U., Wolff, C. and Näther, C. (1999), *Eur. J. Org. Chem.*, 2327–2335.
- [23] Job, P. (1928), *Ann. Chim.* **9**, 113–135.
- [24] Gelbert, M. (1995) Ph. D. thesis (Universität Freiburg, Germany).