Tris(1,10-phenanthroline)iron(II) Complexes. Influence of 4,7-Donor Substitution on the Redox Potential [1]

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Z. Naturforsch. 49b, 675–682 (1994); received December 6, 1993

Redox Potential, Cyclic Voltammetry, Electron Transfer, Kinetics with Chlorine

Several new 4,7-donor substituted 1,10-phenanthrolines were synthesized and the corresponding tris(1,10-phenanthroline)iron(II) complexes were studied by cyclic voltammetry. All iron(II) complexes showed fully reversible waves at scan rates between 50 and 500 mV/s. For some redox systems the kinetics in their reaction with chlorine was studied. Complexes 7k and 7l significantly extend the potential range of tris(1,10-phenanthroline)iron(II) complexes.

Our search for redox active sensoric materials and our continued interest in developing new reactions [2] by applying electron transfer concepts has emphasized the necessity to prepare a series of structurally related, stable one-electron redox systems that exhibit a broad variation in their potentials. In particular for the rational development of oxygen and chlorine sensors based on one-electron oxidation/reduction processes, redox systems (Mn+/M(n+1)+) with neatly spaced potentials are highly desirable.

\[
\begin{align*}
\text{1/2 Cl}_2 + \text{M}^{n+} & \rightarrow \text{Cl}^- + \text{M}^{(n+1)+} \\
\text{O}_2 + \text{M}^{n+} & \rightarrow \text{O}_2^- + \text{M}^{(n+1)+}
\end{align*}
\]

To some extent, triarylamines and their cation radicals fulfill the desired criteria, since by variation of the substituent pattern in the aromatic rings, a whole series of redox systems was synthesized by Steckhan that cover the wide potential range from 0.51–1.72 V vs. SCE [3]. Unfortunately, the triarylamine/triarylamine cation radical redox systems display three decisive disadvantages for their use as sensoric materials: (1) not all the cation radical salts prove to be sufficiently stable [4], especially in the presence of nucleophiles [4, 5], (2) the oxidized form reacts readily with radicals [6], and (3) the reduced form is highly unsoluble in water, which would be the solvent of choice. As an alternative we have decided to investigate Fe(II)/Fe(III)-tris(1,10-phenanthroline) redox systems, since (1) these are much more stable towards nucleophilic attack [7], (2) they are much slower in their reaction with radicals [8], (3) the Fe(II) complexes can readily be analyzed by their strong absorbance around 500 nm [7] and (4) they are water soluble if a proper counter ion is chosen [7]. In order to speed up the response time in chlorine/oxygen sensors, stable systems with relatively low potential (<0.5 V vs. SCE) are needed.

Despite the fact that substituted iron(II)-1,10-phenanthrolines (ferroins) have been playing an important role in analytical chemistry [7] and that ruthenium(II)-1,10-phenanthrolines have attracted wide interest due to their potential for solar energy conversion [9, 10], relatively little effort has been undertaken to influence the electronic situation of the complex by variation of the substituents. A straightforward reason for this neglect is the difficulty to synthesize the corresponding substituted 1,10-phenanthrolines by a simple strategy.

For a moderate number of examples, a variation of the redox potential of tris(1,10-phenanthroline)iron(II) complexes has been observed when the electron density in the 1,10-phenanthroline ligands was changed [8, 11]. However, only a very narrow range of potentials (0.4–0.9 V vs ferrocene) was measured in acetonitrile [8, 11]. According to a simple VB description the strongest influence on the electron density of the N-donor atoms should be exerted by substituents in the positions 2, 4, 7 and 9. But since substitution in 2- and/or 9-positions does hinder complex formation with tran-
transition metals by steric effects, in many cases the corresponding tris(1,10-phenanthroline)iron(II) complexes are not formed any more [8]. Therefore, to alter the electronic properties of tris(1,10-phenanthroline)iron(II) complexes, substitution in 4- and 7-position with electron donating substituents seemed to be the method of choice. Interestingly, only a limited number of 4,7-disubstituted 1,10-phenanthrolines (R = -OMe [12], -OPh [12], -NH₂ [12, 13], -NHR⁺ [13-17]) is known in the literature. But the effect of 4,7-substitution on the oxidation potential of corresponding iron(II)-tris-chelates was not studied in the amino cases. Herein, we report on the synthesis of some new aryloxy- and alkylamino substituted 1,10-phenanthrolines 1 and describe the effect of the substitution on the oxidation potentials of the corresponding iron(II)-tris-chelates.

![Diagram of 1,10-phenanthroline structure]

There are two general pathways to obtain 4,7-donor substituted 1,10-phenanthrolines 1: (1) the de novo synthesis of the 1,10-phenanthroline system from diaminobenzenes and appropriately substituted C₃-units or (2) the modification of an already existing 1,10-phenanthroline, for instance by substitution. For the latter method, a key compound is 4,7-dichloro-1,10-phenanthroline (1c) [15, 16] which itself is accessible via route (1). In a five-step synthesis, 1c can be synthesized from 1,2-diaminobenzene (2) and diethyl ethoxymethylene malonate (3) [15, 16]. An analogous route gives the 4,7-dibromosubstituted 1,10-phenanthroline 1d [18]. The chlorine atoms in compound 1c can be replaced via nucleophilic substitution by a variety of other substituents, like alkoxy, aryloxy and amino groups. Table I lists all 4,7-disubstituted 1,10-phenanthrolines 1 synthesized in this work and the ¹H NMR signals of the 1,10-phenanthroline moiety. The ¹H NMR and all other analytical data support the assignment of 4,7-substituted 1,10-phenanthrolines 1.

Using the new 1,10-phenanthrolines 1 listed in Table I, we have synthesized the corresponding iron(II) complexes using a modification of a literature procedure [11]. Thus, a solution of the 1,10-phenanthrolines 1f–11 in acetonitrile/water was reacted with FeSO₄·7 H₂O and from the intensely red-colored solutions the red salts were precipitated by addition of ammonium hexafluorophosphate. The complexes were identified by their characteristic, strong UV absorbance between
490–495 nm and by the $^1\text{H}$ NMR spectra. Unfortunately, according to elemental analysis the iron(II) complexes prepared by this precipitation strategy always contained small amounts of the iron(III) tris-chelates (presumably by air oxidation). The presence of small amounts of paramagnetic Fe(III) complexes may also be inferred from the broadening of the $^1\text{H}$ NMR signals. Since iron(III) impurities do not cause problems in the cyclic voltammetry study all new systems were prepared by the ammonium hexafluorophosphate precipitation route. The red complexes 77k and 77l proved to be extremely air-sensitive, but they could be handled in the presence of an added reductant, like hydroxylamine or hydrazine. Likewise, the oxidized form of 77l (green) could be reduced to the red iron(II) state by careful addition of a hydrazine solution in acetonitrile and reoxidized by Ce(IV).

In cyclic voltammetry investigations (CV), all iron(II)/iron(III) redox couples exhibited clean and completely reversible waves (between 50–500 mV/s) and fulfilled other criteria for complete reversibility: (1) $E_{1/2}$ is independent of the scan rate; (2) the peak current ratio $i_{pc}/i_{pa}$ is unity; (3) the separation of the cathodic and anodic peaks is $60 \pm 5$ mV (Table II) and (4) $i_{pa}/v^{1/2}$ is constant.

When the aryloxy substituted iron 1,10-phenanthrolines 77f–i are compared within the series no major shift of the oxidation potentials was observed reflecting the small range of oxidation potentials of the 1,10-phenanthroline ligands themselves ($\Delta E_{pa} = 0.1$ V). This outcome is surprising when considering that the substituents R at the phenanthroline 1 usually entail a much larger oxidation potential difference when being attached to a methyl group (e.g. $\Delta E_{ox} = 0.37$ V for 4-methoxy-

Table II. Cyclic voltammetry data and redox potentials $E_{1/2}$ of tris(1,10-phenanthroline)iron(II)hexafluorophosphates 77·(PF$_6$)$_2$ in acetonitrile and anodic peak potentials $E_{pa}$ for the ligands 1.

<table>
<thead>
<tr>
<th>7</th>
<th>Substituent in 4,7-position</th>
<th>$E_{1/2}$ (7) $E_{pa}$ (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>H</td>
<td>0.69 1 57 &gt;2</td>
</tr>
<tr>
<td>7e</td>
<td>OMe</td>
<td>0.38 1 55</td>
</tr>
<tr>
<td>7b</td>
<td>O-p-C$_6$H$_5$</td>
<td>0.47 1 60</td>
</tr>
<tr>
<td>7e</td>
<td>O-p-C$_6$H$_5$–OMe</td>
<td>0.45 1 60</td>
</tr>
<tr>
<td>7f</td>
<td>O-p-C$_6$H$_5$–tBu</td>
<td>0.47 1 60</td>
</tr>
<tr>
<td>7j</td>
<td>O-(1-naphthyl)</td>
<td>0.49 1 60</td>
</tr>
<tr>
<td>7k</td>
<td>NH(CH$_2$)$_3$NH$_2$</td>
<td>0.23 1 60</td>
</tr>
<tr>
<td>7l</td>
<td>NEt$_2$</td>
<td>-0.09 1 60</td>
</tr>
</tbody>
</table>

a All potentials are referenced to ferrocene which itself has $E_{1/2} = +0.39$ V vs. SCE; $^b$ ratio of the anodic to cathodic peak current of 7; $^c$ peak to peak separation of 7; $^d$ anodic peak potentials; $^e$ no anodic peak was detected up to 2 V; $^f$ a strong coating of the electrode occurred during the anodic sweep.

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Table I. 4,7-Disubstituted 1,10-phenanthrolines 1.

<table>
<thead>
<tr>
<th>1</th>
<th>R</th>
<th>Yield (%)</th>
<th>Synthesized from</th>
<th>$^1\text{H}$ NMR (250 MHz, CDCl$_3$)</th>
<th>d. 2H (J in Hz)</th>
<th>s. 2H (J in Hz)</th>
<th>d. 2H (J in Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>-</td>
<td>Commercially available</td>
<td>[19]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1b</td>
<td>Me</td>
<td>4</td>
<td>[2] [19]</td>
<td>7.49 (5)</td>
<td>8.06</td>
<td>9.08 (5)</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>Cl</td>
<td>31</td>
<td>[2] [16]</td>
<td>7.77 (4.5)</td>
<td>8.35</td>
<td>9.09 (4.5)</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>Br</td>
<td>10</td>
<td>[2] [18]</td>
<td>7.94 (4.5)</td>
<td>8.27</td>
<td>8.93 (4.5)</td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>OMe</td>
<td>76</td>
<td>[1] [12]</td>
<td>7.0 (4.5)</td>
<td>8.2</td>
<td>9.0 (4.5)</td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>O$_2$C$_6$H$_5$</td>
<td>55</td>
<td>[1] [12]</td>
<td>6.85 (6)</td>
<td>8.39</td>
<td>8.94 (6)</td>
<td></td>
</tr>
<tr>
<td>1g</td>
<td>O-p-C$_6$H$_5$Me</td>
<td>73</td>
<td>[1] [12]</td>
<td>6.80 (5.3)</td>
<td>8.38</td>
<td>8.93 (5.3)</td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>O-p-C$_6$H$_5$Bu</td>
<td>85</td>
<td>[1] [12]</td>
<td>6.84 (5)</td>
<td>8.38</td>
<td>8.92 (5)</td>
<td></td>
</tr>
<tr>
<td>1i</td>
<td>O-p-C$_6$H$_5$OMe</td>
<td>70</td>
<td>[1] [12]</td>
<td>6.79 (5.3)</td>
<td>8.41</td>
<td>8.93 (5.3)</td>
<td></td>
</tr>
<tr>
<td>1j</td>
<td>O-(1-naphthyl)</td>
<td>40</td>
<td>[1] [12]</td>
<td>6.82 (4.5)</td>
<td>8.74</td>
<td>9.10 (4.5)</td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>NH(CH$_2$)$_3$NH$_2$</td>
<td>72</td>
<td>[1] [12]</td>
<td>6.66 (6.0)</td>
<td>8.00</td>
<td>8.54 (6.0)</td>
<td></td>
</tr>
<tr>
<td>1l</td>
<td>NEt$_2$</td>
<td>16</td>
<td>[1] [12]</td>
<td>7.02 (7.2)</td>
<td>7.83</td>
<td>9.02 (7.2)</td>
<td></td>
</tr>
</tbody>
</table>

a In CD$_3$CD$_2$OD.
toluene and 1,4-dimethoxybenzene [20]), but this difference cannot be found in the substituted 1,10-phenanthrolines 1g and 1i.

On the other hand, the diamino substituted iron 1,10-phenanthroline complexes 7k ($E_{1/2} = -0.23$ V vs. ferrocene) and 7l ($E_{1/2} = -0.09$ V vs. ferrocene) revealed quite pronounced substituent effects on the redox potentials. In the CV investigation both, 7k and 7l, exhibited fully reversible waves in acetonitrile, but interestingly, the cyclic voltammogram of 7l showed, beside the reversible Fe(II)/Fe(III) redox process, a second reversible wave at $E_{1/2} = 0.95$ V vs. ferrocene that was followed by an irreversible one at $E_{pa} = 1.19$ V (see Fig. 1). In the presence of tris(4-bromophenyl)amine as internal reference and at higher scan rates ($v = 0.5$ V/s) the wave at 1.19 V exhibited some reversibility ($E_{1/2} = 1.14$ V). A control experiment proved that the ligand 11 itself, which can be regarded as a vinylogous Wurster type system, was oxidized irreversibly at $E_{pa} = 0.71$ V. Thus, we ascribe the reversible wave at $E_{1/2} = -0.09$ V to an Fe(II)–Fe(III) redox process, while the reversible wave at $E_{1/2} = 0.95$ V and the partially reversible one at $E_{1/2} = 1.14$ V are supposed to correspond to formation of ligand cation radicals. It is noteworthy that the irreversible oxidation wave in 11 ($E_{pa} = 0.71$ V) becomes reversible in the iron tris-chelate ($E_{1/2} = 0.95$ V), a process not understood at present.

In order to probe these Fe(II)/Fe(III) complexes as potential materials in gas sensors, we have undertaken a kinetic analysis of the reduction of chlorine using the redox systems 7e, 7g, 7j and 7k.

$$\text{Fe}^{II}(\text{I})_3 + 1/2 \text{Cl}_2 \rightarrow \text{Fe}^{III}(\text{I})_3 + \text{Cl}^-$$

The kinetics were followed at 25°C under pseudo-first order conditions in methylene chloride/CCl₄, since in acetonitrile/CCl₄ or water the reaction was too fast to be monitored by our setup (Table III). But even in methylene chloride/CCl₄, the reaction of 7k with chlorine was too rapid to be measured. This suggests that 4,7-substitution of the ligand with amino groups should lead to an improvement of the response time of the corresponding iron(II) 1,10-phenanthroline complexes in the reaction with chlorine.

The easily oxidizable 7k not only has significantly extended the range of oxidation potentials of iron(II)1,10-phenanthroines 7 but also is much more rapid in its reaction with chlorine. To assess the general potential for their use in sensors, other donor substituted 1,10-phenanthrolines are under current investigation. In addition, mixed-ligand complexes [21] should allow to access the potentials between -0.23 and 0.35 V. Since these structurally related compounds most likely constitute outer-sphere one-electron oxidants they may serve

Fig. 1. Cyclic voltammetry study of 1,10-phenanthroline 11 (trace a) and complex 7l (trace b and c) in acetonitrile at a scan rate of 100 mV/s.
Table III. Kinetic data for the reduction of chlorine by the iron(II) complexes 7 (at 25 °C).

<table>
<thead>
<tr>
<th>7</th>
<th>R</th>
<th>( E_{1/2} ) (solvent [V])</th>
<th>( \tau_{1/2}^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7e</td>
<td>OMe</td>
<td>0.35 CH₂Cl₂/CCl₄ 5 min</td>
<td></td>
</tr>
<tr>
<td>7g</td>
<td>O-p-C₆H₄-Me</td>
<td>0.45 CH₂Cl₂/CCl₄ 64 min</td>
<td></td>
</tr>
<tr>
<td>7j</td>
<td>O-(1-naphthyl)</td>
<td>0.49 CH₂Cl₂/CCl₄ 36 min</td>
<td></td>
</tr>
<tr>
<td>7k</td>
<td>NH(CH₂),₂NH₂</td>
<td>-0.23 CH₂Cl₂/CCl₄ upon mixing</td>
<td></td>
</tr>
<tr>
<td>7l</td>
<td>O-(1-naphthyl)</td>
<td>0.49 CH₂CN/CCl₄ several s</td>
<td></td>
</tr>
</tbody>
</table>

\( \tau_{1/2}^a \) Half time for the disappearance of iron(II) complexes 7.

as important mechanistic probes for testing the involvement of cation radicals in electron transfer reactions [22].

**Experimental**

General remarks: see [22, 23]. The cyclic voltammograms of all the Fe(II)/Fe(III) couples were measured using a standard three electrode set-up (Pt working at Pt auxiliary electrode, silver wire as reference electrode) hooked up to a Princeton Applied Research Model 362 potentiostat. The cyclic voltammograms of all the Fe(II)/Fe(III) couples were measured using a standard three electrode set-up (Pt working at Pt auxiliary electrode, silver wire as reference electrode) hooked up to a Princeton Applied Research Model 362 potentiostat. The ferrocene/ferrocenium couples exhibit \( E_{1/2} = +0.39 \) V vs. SCE under our conditions. The oxidation potentials of 11 and 71 were originally measured against internal ferrocene for practical reasons. The ferrocene/ferrocenium couple exhibits \( E_{1/2} = +0.70 \) V vs. ferrocene. 4,7-Dichloro-1,10-phenanthroline (1e) was prepared according to the procedure described by Snyder and Freier [16]. Complexes 7a and 7e are described in ref. [4, 11].

4,7-Dimethoxy-1,10-phenanthroline (1e): 0.75 g (32 mmol) of sodium was dissolved in ca. 50 ml of dry methanol. Then at room temp. 1.0 g (4.0 mmol) of 4,7-dichloro-1,10-phenanthroline (1c) was added and the mixture was refluxed for 1 h. The methanol was distilled off, 30 ml of dichloromethane was added, the solution was washed with 30 ml of water and the organic layer was dried with MgSO₄. After evaporation of the solvent, the residue was recrystallized from 50 ml of toluene yielding 0.73 g (76%) of 1e (23% [12]), m.p. 209 °C (209–210 °C [12]). – IR (KBr): \( \nu = 1580, 1560, 1500 \) cm\(^{-1}\) (arom.). 1280, 1220, 1025 (C–O). – \(^1\)H NMR (250 MHz, CDCl₃):

\[ \delta = 4.1 \text{ (s, 6H)}, 7.0 \text{ (d, } J = 4.5 \text{ Hz, 2H)}, 8.2 \text{ (s, 2H)}, 9.0 \text{ (d, } J = 4.5 \text{ Hz, 2H}). – MS (70 eV): m/z (\%) = 240 (100), 225 (26), 210 (6). \]

4,7-Bis(4-methylphenoxy)-1,10-phenanthroline (1g): In a flask fitted with a drying tube, 2.00 g (8.00 mmol) of 4,7-dichloro-1,10-phenanthroline (1c), 11.80 g (110.0 mmol) of 4-nitrophenol and 4.5 g (80 mmol) of 4,7-dichloro-1,10-phenanthroline (1c), 33.0 g (220 mmol) of 4-tert-butylphenol and 4.5 g (80 mmol) of powdered KOH was stirred at 130 °C for 22 h. The dark brown reaction product was dissolved in 100 ml of 30% KOH and extracted six times with 50 ml of dichloromethane. The combined organic layer was washed twice with 50 ml of 2 N NaOH and twice with 60 ml of water. After drying with MgSO₄, the solvent was evaporated, and the brown solid residue was recrystallized first from aqueous ethanol, then from methylene chloride yielding 2.30 g (73%) of 1g, m.p. 256–257 °C. – IR (KBr): \( \nu = 3050 \) cm\(^{-1}\), 1613, 1586, 1557, 1491 (arom.), 1273, 1231, 1202, 1023 (C–O), 916, 839 (arom.). – \(^1\)H NMR (250 MHz, CDCl₃): \( \delta = 2.40 \text{ (s, 6H)}, 6.80 \text{ (d, } J = 5.3 \text{ Hz, 2H}), 7.10 \text{ (m, 4H)}, 7.27 \text{ (m, 4H)}, 8.38 \text{ (s, 2H)}, 8.93 \text{ (d, } J = 5.3 \text{ Hz, 2H}). – ^{13}C\text{ NMR (100 MHz, CDCl₃): } \delta = 20.9 \text{ (C-7', C-7''), 107.0 \text{ (C-3, C-8), 119.5 \text{ (C-5, C-6), 120.8 \text{ (C-2', C-6'), 121.3 \text{ (C-4-a, C-6-a), 130.8 \text{ (C-3', C-5'), 135.5 \text{ (C-4', C-4'\text{), 147.4 \text{ (C-1-a, C-10-a, 151.0 \text{ (C-2, C-9), 152.1 \text{ (C-1', C-1'\text{, 162.2 \text{ (C-4, C-7). – MS (70 eV): m/z (\%) = 392 (100), 377 (15), 285 (11), 270 (5), 195 (10), 91 (17), 84 (7), 65 (18).}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}} \]

C₂₆H₂₅N₂O₂
Calcd 392.1518,
Found 392.1525.

C₂₆H₂₅N₂O₂ · 1/4 H₂O (396.6)
Calcd C 78.74 H 5.21 N 7.06,
Found C 78.64 H 5.08 N 7.05.
4,7-Bis(1,1-dimethylethyl)-phenoxy-1,10-phenanthroline (1h): 4.10 g (16.5 mmol) of 4,7-dichloro-1,10-phenanthroline (1c), 33.0 g (220 mmol) of 4-tert-butyl phenol and 4.5 g (80 mmol) of powdered KOH were melted at 130 °C and stirred for 11 h. At room temp, the product was dissolved in 30% KOH and extracted with dichloromethane (3 times 80 ml). After washing the combined organic layers with 80 ml of 2 N NaOH and 80 ml of water and drying with MgSO₄, the solvent was evaporated. The residue was recrystallized from ethanol yielding 6.67 g (85%) of 1h, m.p. 233 °C. – IR (KBr): \( \nu = 2945 \) cm\(^{-1}\), 1581, 1553, 1490 (arom.), 1282 (C–O). – \(^1\)H NMR (250 MHz, CDCl₃): \( \delta = 1.37 \text{ (s, 18H)}, 6.84 \text{ (d, } J = 5 \text{ Hz, 2H)}, 7.14 \text{ (d, } J = 9 \text{ Hz, 4H)}, 7.49 \text{ (d, } J = 9 \text{ Hz, 4H)}, 8.38 \text{ (s, 2H)}, 8.92 \text{ (d, } J = 5 \text{ Hz, 2H}). – MS (70 eV): m/z (\%) = 476 (88), 461 (100), 405 (23).
C$_{32}$H$_{32}$N$_2$O$_2$ (322.45)
Calcd  C 80.64  H 6.76  N 5.87,
Found  C 80.45  H 6.70  N 5.84.

4,7-Bis(4-methoxyphenoxy)-1,10-phenanthroline (11): In a flask fitted with a drying tube, 1.70 g (6.7 mmol) of 4,7-dichloro-1,10-phenanthroline (1c), 11.50 g (92.0 mmol) of 4-hydroxyanisol and 1.90 g (35.5 mmol) of powdered KOH were stirred at 110 °C for 21 h. After work-up analogous to 1g, the resulting slightly brown solid was recrystallized first from toluene, then from methylene chloride yielding 2.00 g (70%) of 4,7-dichloro-l,10-phenanthroline 1, m.p. 203 °C. - IR (KBr): ν = 3056 cm$^{-1}$ (arom.), 2831 (OCH$_3$), 1611, 1586, 1558, 1491 (arom.), 1377, 1321, 1201, 1042 (C – O), 916, 843 (arom.). - 1H NMR (250 MHz, CDCl$_3$): δ = 3.87 (s, 6 H), 6.79 (d, J = 5.3 Hz, 2 H), 7.02 (m, 4 H), 7.18 (m, 4 H), 8.41 (s, 2 H), 8.93 (d, J = 5.3 Hz, 2 H). - 13C NMR (100 MHz, CDCl$_3$): δ = 55.7 (C – 7, C – 7''), 106.6 (C – 3, C – 3'), 115.4 (C – 3', C – 3'', C – 3'), 120.0 (C – 5, C – 6), 121.2 (C – 4a, C – 6a), 122.2 (C – 2', C – 6', C – 2'', C – 6''), 147.1 (C – 1a, C – 10a), 147.6 (C – 1', C – 1''), 147.0 (C – 2, C – 9), 157.4 (C – 4', C – 4''), 162.6 (C – 4, C – 7). - MS (70 eV): m/z (%) = 424 (100), 301 (18), 285 (6), 212 (8), 178 (23).

C$_{26}$H$_{20}$N$_2$O$_4$·1/4 H$_2$O (429.0)
Calcd C 72.80 H 4.82 N 6.53,
Found C 72.63 H 4.65 N 6.58.

4,7-Bis(1-naphthoxy)-1,10-phenanthroline (1j): In a flask fitted with a drying tube, 2.00 g (8.0 mmol) of 4,7-dichloro-1,10-phenanthroline (1c), 15.8 g (110 mmol) of 1-naphthol and 2.25 g (40.0 mmol) of powdered KOH were stirred at 125 °C for 7.5 h. The darkbrown product as dissolved in 150 ml of 30% KOH, and extracted with dichloromethane for 5 d. The darkgreen organic layer was washed three times with 60 ml of 30% KOH, three times with 100 ml of 2 N NaOH, and twice with 100 ml of water. After drying with MgSO$_4$ and evaporation of the solvent, the residue was recrystallized from aqueous ethanol, yielding 1.5 g (40%) of 1j, m.p. 203 °C. - IR (KBr): ν = 3046 cm$^{-1}$, 1591, 1559, 1499 (arom.), 1265, 1239 (C – O), 921, 841, 813 (arom.). - 1H NMR (250 MHz, CDCl$_3$): δ = 6.82 (d, 2 H, J = 4.5 Hz), 7.39 (dd, 2 H, J$_1$ = 6.75 Hz, J$_2$ = 1.0 Hz), 7.49 (m, 4 H), 7.59 (dt, 4 H, J$_1$ = 9.0 Hz, J$_2$ = 1.0 Hz), 7.87 (d, 2 H, J = 9.0 Hz), 7.91 (d, 2 H, J = 9.0 Hz), 8.00 (d, 2 H, J = 9.0 Hz), 8.74 (s, 2 H), 9.10 (d, 2 H, J = 4.5 Hz). - 13C NMR (100 MHz, CDCl$_3$): δ = 107.43 (C – 3, C – 8), 117.15 (C – 2', C – 2''), 119.84 (C – 5, C – 6), 121.34 (C – 4a, C – 6a), 121.60, 125.87, 125.95, 126.14, 126.89, 127.09, 128.33, 135.37 (C – 10'), 147.36 (C – 1a, C – 10a), 150.23 (C – 1', C – 1''), 151.30 (C – 2, C – 9), 162.43 (C – 4, C – 7). - MS (70 eV): m/z (%) = 464 (100), 335 (9), 321 (9), 232 (6), 195 (6), 127 (37), 115 (18), 77 (8).

C$_{32}$H$_{32}$N$_2$O$_2$ (464.0)
Calcd C 82.75 H 4.32 N 6.03,
Found C 82.90 H 4.33 N 6.10.

4,7-Bis(3-aminopropylamino)-1,10-phenanthroline (1k): 0.40 g (1.6 mmol) of 4,7-dichloro-1,10-phenanthroline (1c) and 4.7 g (63 mmol) of 1,3-diaminopropane were stirred for 3.5 h at 140 – 150 °C. The beige-colored product was filtered off, washed several times with chloroform and dried in vacuo, yielding 0.38 g of 1k (72%), m.p. 117 – 136 °C (decomposition). - IR (KBr): ν = 2920 cm$^{-1}$, 1580, 1420, 1320. - 1H NMR (250 MHz, CD$_2$CD$_2$OD): δ = 1.91 (quint., J = 7.2 Hz, 4 H), 2.81 (t, J = 7.2 Hz, 4 H), 3.42 (t, J = 7.2 Hz, 4 H), 5.29 (br. s, H$_2$O/OH and NH/NH$_2$), 6.66 (d, J = 6.0 Hz, 2 H), 8.00 (s, 2 H), 8.54 (d, J = 6.0 Hz, 2 H). - MS (70 eV): m/z (%) = 324 (45), 294 (78), 280 (100), 235 (41), 223 (44).

C$_{18}$H$_{32}$N$_6$S
Calcd 324.2062,
Found 324.2057.

C$_{18}$H$_{34}$N$_6$·H$_2$O (342.45)
Calcd C 63.14 H 7.65 N 24.54,
Found C 62.83 H 6.98 N 23.97.

4,7-Bis(diethylamino)-1,10-phenanthroline (1l): 2.5 g (9.4 mmol) of 4,7-dichloro-1,10-phenanthroline (1c) and 100 ml of diethylamine were shaken in an autoclave at 120 °C for 20 h. At room temp. the volatiles were evaporated in vacuo, the residue was dissolved in 200 ml of dichloromethane and washed twice with 60 ml of 2 N NaOH and twice with 50 ml of water. After drying with MgSO$_4$, the solvent was evaporated and the residue was recrystallized from acetone, yielding 0.5 g (16%) of 1l, m.p. 131 °C. - IR (KBr): ν = 1594 cm$^{-1}$, 1555, 1500 (arom.). - 1H NMR (250 MHz, CDCl$_3$): δ = 1.33 (t, J = 7.2 Hz, 12 H), 3.61 (q, J = 7.2 Hz, 8 H), 7.02 (d, J = 7.2 Hz, 2 H), 7.83 (s, 2 H), 9.02 (d, J = 7.2 Hz, 2 H). - MS (70 eV): m/z (%) = 322 (84), 307 (100), 278 (68).

C$_{26}$H$_{26}$N$_4$ (322.45)
Calcd C 74.49 H 8.12 N 17.37,
Found C 74.22 H 8.07 N 17.32.

General procedure for the preparation of the tris-[4,7-disubstituted-1,10-phenanthroline]iron(II)-hexafluorophosphates (7)

1.28 mmol of a 4,7-disubstituted-1,10-phenanthroline 1 was added to a solution of 0.55 mmol...
of iron(II)-sulfate heptahydrate in 10 ml of distilled water, and the red suspension was sonicated with ultrasound for 30 min at 60 °C. Addition of 5 ml of acetonitrile gave a deep-red, clear solution, from which the precipitate was collected after addition of 1.00 mmol of ammonium hexafluorophosphate. The red solid was filtered off, washed with 80 ml of distilled water and dried at 120 °C in vacuo.

Tris-(4,7-diphenoxy-1,10-phenanthroline)iron(II)-hexafluorophosphate (7f): Yield: 95%. – IR (KBr): v = 3055 cm⁻¹, 1617, 1607, 1575, 1414, 1290, 1236, 1207, 926, 835. – UV (CH₃CN): λ_max = 490 nm. – ¹H NMR (250 MHz, CDC1₃): δ = 6.98 (br. s, 6 H), 7.24 (br. m, 18 H), 7.46 (br. s, 12 H), 7.67 (br. s, 6 H), 8.50 (br. s, 6 H).

Tris-(4,7-bis-(methylphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7g): Yield: 97%. – IR (KBr): v = 3025 cm⁻¹, 2951, 1627, 1600, 1576, 1496, 1414, 1290, 1236, 1207, 926, 850. – UV (CH₃CN): λ_max = 492 nm. – ¹H NMR (250 MHz, CDC1₃): δ = 2.34 (br. s, 18 H), 6.95 (br. s, 6 H), 7.07 (br. m, 12 H), 7.24 (br. m, 12 H), 7.60 (br. s, 6 H), 8.46 (br. s, 6 H).

Tris-(4,7-bis-(4,1-dimethylphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7h): Yield: 96%. – IR (KBr): v = 3085 cm⁻¹, 2950, 2860, 1630, 1576, 1495, 1415, 1250, 1237, 1216, 926, 850. – UV (CH₃CN): λ_max = 495 nm. – ¹H NMR (250 MHz, CDC1₃): δ = 1.30 (br. s, 54 H), 6.98 (br. s, 6 H), 7.12 (br. s, 12 H), 7.44 (br. s, 12 H), 7.64 (br. s, 6 H), 8.46 (br. s, 6 H).

Tris-(4,7-bis-(4-methoxyphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7i): Yield: 97%. – IR (KBr): v = 3075 cm⁻¹, 2985, 2935, 2825, 1625, 1607, 1575, 1492, 1410, 1288, 1251, 1233, 1205, 1035, 924, 845. – UV (CH₃CN): λ_max = 490 nm. – ¹H NMR (250 MHz, CDC1₃): δ = 3.80 (br. s, 18 H), 6.94 (br. s, 18 H), 7.12 (br. m, 12 H), 7.62 (br. s, 6 H), 8.48 (br. s, 6 H).

Tris-(4,7-bis-(1-naphthoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7j): Yield: 77%. – IR (KBr): v = 3045 cm⁻¹, 1625, 1600, 1573, 1413, 1392, 1285, 1265, 1235, 923, 845. – UV (CH₃CN): λ_max = 495 nm. – ¹H NMR (250 MHz, CDC1₃): δ = 6.96 (br. s, 6 H), 7.48 (br. m, 24 H), 7.86 (br. m, 24 H), 8.72 (br. s, 6 H).

Tris-(4,7-bis-(4-aminobenzylphenoxy)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7k): Yield: 75%. – IR (KBr): v = 3434 and 3384 (NH, NH₂) cm⁻¹, 2909, 2829, 1614, 1569, 1559, 1429, 1383, 1339, 1309, 1237, 1144, 1124, 1113, 1091, 729, 639, 630. – UV (CH₃CN): λ_max = 505 and 524 nm (broad). – ¹H NMR (250 MHz, CD₂OD): δ = 2.03 (br. m, 12 H), 3.07 (br. m, 12 H), 3.48 (br. m, 12 H), 6.75 (br. s, 6 H), 7.30 (br. m, 6 H), 8.15 (br. m, 6 H).

Tris-(4,7-bis-(diethylamino)-1,10-phenanthroline)iron(II)-hexafluorophosphate (7l) was only prepared in situ in the presence of hydrazine to avoid air oxidation.

**Kinetic measurements**

One chamber of a tandem cuvette was filled with 1.20 ml of a 2·10⁻⁴ M solution of 7 (either in acetonitrile or methylene chloride) and the other chamber was filled with an equal amount of a chlorine solution (2.3 M) in CCl₄ [24]. After mixing, the absorbance was followed at λ_max of the iron(II)-1,10-phenanthroline for at least 3 half times and showed pseudo-first order behavior.

We wish to thank Prof. Dr. C. Ruchardt for his generous support of this work. The financial help of the Fonds der Chemischen Industrie and the Landesschwerpunkt “Elektroaktive Systeme für die Sensorik” (Freiburger Sensor-Verbund) is gratefully acknowledged.

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