Synthesis and Spectroscopy of New Iron(II) Complexes of 4,7-Bis(aza-crown ether)-phenanthrolines with Unusual Complexation Properties

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Novel aza-crown ether-phenanthroline iron(II) complexes have been prepared and their recognition of group 1/2 metal cations investigated by NMR and electroanalysis, indicating a remarkable reorganisation within the Ba^{2+}/crown ether subunits of **4c** at a higher concentration of the group 2 cation.

Despite the important role that metal phenanthroline complexes have played in analytical chemistry[1] and solar energy conversion,[2,3] very little work has been undertaken to control the electronic properties of the complexes by variation of the substituents in the 4,7-position. Recently, in our search for new electroactive catalysts and sensor materials we have demonstrated that the introduction of amino groups in the 4,7-position of 1,10-phenanthroline ligands can lead to a decrease in the redox potential of the corresponding iron(II) trisphenanthroline complexes by more than 0.9 V compared to the parent system.[4] Hence, inspired by the investigations of Beer *et al.*[5] on aza-crown ether linked bipyridyl metal complexes[6] and on their ability to recognise group 1 and 2 metal cations we became curious about whether the direct attachment of aza-crown ethers in the 4,7-position of the phenanthroline ligands would lead to an amplification of sensoric effects because of having six crown ether subunits electronically linked to one redox centre.

The reaction of excess aza-crown ethers **1a–c** with 4,7-dichlorophenanthroline **2** at 150–160 °C provided the aza-crown ether phenanthroline ligands **3a–c** in 79, 69 and 63% yield, respectively (Scheme 1). On the basis of spectroscopic evidence the structures of the new ligands were unequivocally authenticated. Finally, the corresponding iron(II) complexes **4a–c** were obtained from the reaction of ligands **3a–c** with $FeSO_4 \cdot 7H_2O$ in water followed by precipitation of the red salts as hexafluorophosphates or perchlorates in yields of 63, 34 and 64%. The complexes were identified by their characteristic strong UV absorption maxima between 537–545 nm and by ^1H and ^{13}C NMR spectroscopy.[†]

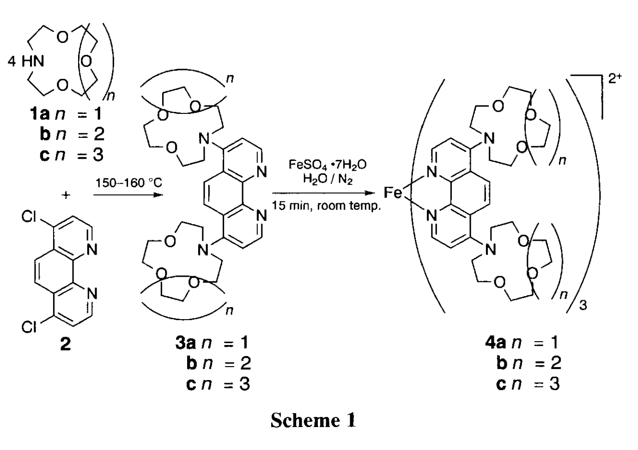
CV investigations on **4a–c** in acetonitrile revealed fully reversible waves for the $Fe^{II} \rightleftharpoons Fe^{III}$ redox transition, as indicated by $i_c/i_a = 1$ and ΔE_p[‡] of 60 mV. The corresponding half-wave potentials $E_{1/2}{}^{ox}$ are placed at 0.40, 0.43 and 0.46 V *vs.* SCE, thus lower than the one of the parent system by about 0.6 V.[4] Direct evidence for the recognition of metal ions by **4a–c** was readily obtained upon examination of the shift of $\Delta E_{1/2}{}^{ox}$ in CV experiments measured in acetonitrile (Table 1).

For all the metal ions described in Table 1 the binding to the aza-crown ethers is only very weak, since from an evaluation of complete data sets (at least 10 different concentrations of metal ions), obtained consistently by $E_{1/2}{}^{ox}$ as well as ^{13}C NMR shifts, low association constants can be inferred. This observation can readily be rationalised by the constraints the aza-crown ether is subjected to when bound directly to 4- and 7-position of the phenanthroline. MM2-calculations indicate that as a result of the interaction with the 5- and 6-H's at the phenanthroline ligand the conformational freedom of the aza-crown ether moieties is severely restricted.

In light of the moderate complex formation constants with the Group 1 metal ions in Table 1 it was surprising to see that the complex of **4c** with Ba^{2+} (using anhydrous $BaClO_4$) proved to be stronger than all the others exhibiting an overall shift of $\Delta E_{1/2}{}^{ox}$ = 370 mV upon addition of only 1 equiv. of the cationic guest. This remarkable shift may be compared with $\Delta E_{1/2}{}^{ox}$ = 60 mV upon addition of 1 equiv. of K^+. Additionally, an interesting phenomenon, which could be monitored equally by CV ($\Delta E_{1/2}{}^{ox}$ and ΔE_p) as well as by ^{13}C NMR spectroscopy showed up, when the Ba^{2+} concentration was increased stepwise.

From the ΔE_p data [Fig. 1(*b*)] we learn that the kinetics of electron transfer at the electrode is dramatically altered upon addition of Ba^{2+}. While ΔE_p is going through a maximum (at around 1 equiv. addition) the heterogeneous electron transfer constant k_{ET} is then at its lowest value.[7] Interestingly, all three measured observables attain a maximum at 1 equiv. addition of Ba^{2+}, then decline and finally level off at about 10 equiv. Unfortunately, we don't know the stoichiometry of the crown ether complex **4c** when 10 equiv. of Ba^{2+} are added, but it is reasonable to assume that all six crown ether moieties of the iron complex are bound to one Ba^{2+} each. This assumption is based on the fact, that $\Delta E_{1/2}{}^{ox}$ with Ba^{2+} is 330 mV thus being roughly double as high as $\Delta E_{1/2}{}^{ox}$ for the K^+ complex (150 mV, Table 1), in line with the simple expectation that the charge to radius value[§] of the incorporated M^+ governs the $\Delta E_{1/2}{}^{ox}$ shift.[5]

To explain the unusual effect of Ba^{2+}-addition we propose the following mechanistic model: upon addition of 1 equiv. of Ba^{2+} most of the crown ether subunits in **4c**, presumably five out of six, are loaded with the Group 2 metal cation. Due to the strong binding of the Ba^{2+}-ions to the nitrogen lone pairs (in the 4- and 7-position of each phenanthroline ligand) heterogeneous electron transfer is slowed down since nitrogen lone pair–electrode overlap is significantly impaired. As a consequence of the notable through-bond interaction between the Fe-centre and the cationic guests the redox potential is raised to a value of 370 mV



Scheme 1

Table 1 Shift of the half-wave potential $\Delta E_{1/2}{}^{ox}$ in **4a–c** with added Group 1 metal cations M^+

System	Metal ion M^+	Equivalents added[a]	$\Delta E_{1/2}{}^{ox}$/mV	Equivalents added[a]	$\Delta E_{1/2}{}^{ox}$/mV
4a	Li^+	10	< 10 mV	250	140
4b	Na^+	10	100 mV	60[b]	150
4c	K^+	10	140 mV	20[b]	150

[a] One equiv. of M^+ is the amount needed to theorectically load all crown ether subunits in iron complex **4**. [b] At these amounts of M^+, no further change in $E_{1/2}{}^{ox}$ is noted and it is assumed that all crown ether subunits are loaded.

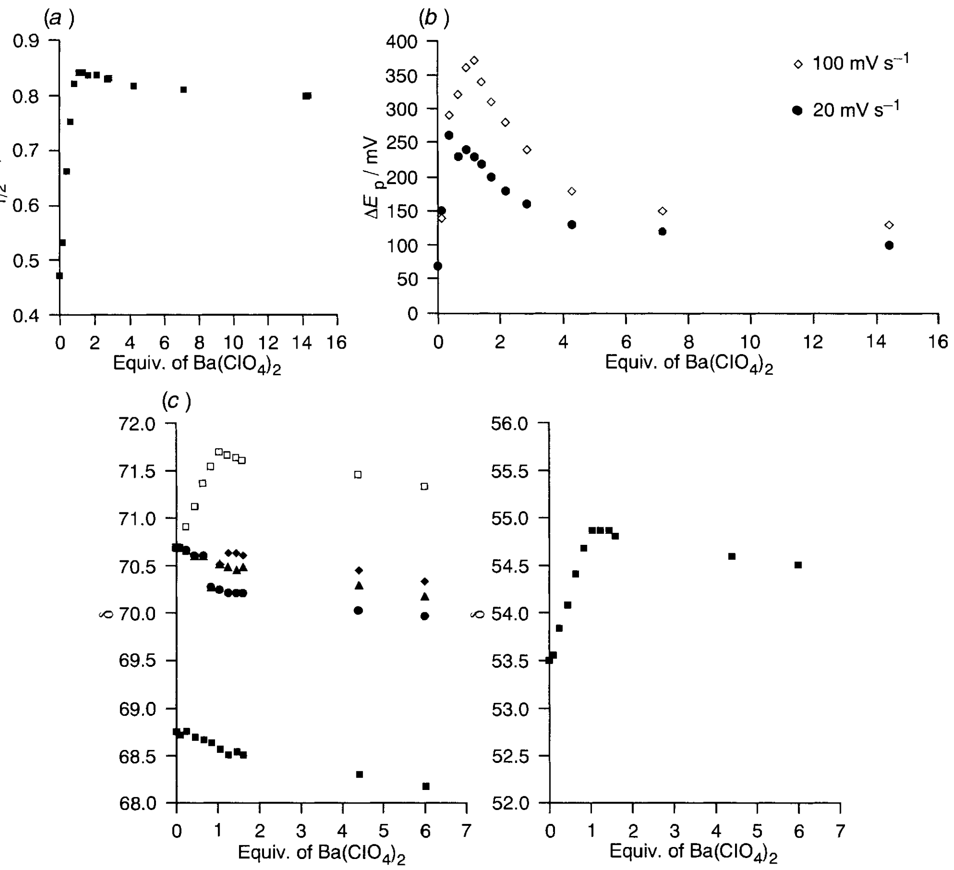


Fig. 1 Effect of Ba^{2+} addition on (*a*) $E_{1/2}^{ox}$ (*b*) ΔE_p and (*c*) the ^{13}C NMR chemical shift of all CH_2-groups (bottom) of iron complex **4c**

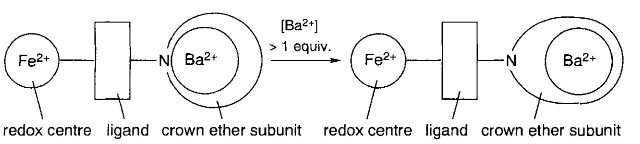


Fig. 2 Schematic representation of the hypothetical Ba^{2+} relocation within the crown ether subunit

above the one of the unloaded trisphenanthroline iron complex. Complexation of a further Ba^{2+} ion, presumably the sixth to the last unloaded crown ether subunit, is now becoming very difficult as a result of substantial Coulomb repulsion. Thus, complexation of the sixth Ba^{2+} is only possible by shifting all the complexed Ba^{2+} ions to the remote periphery of the crown ether (Fig. 2), thereby reducing the Coulomb repulsion term.

This relocation of the cationic guest within the crown ether moiety is indicated by the splitting of three ^{13}C-signals so far isochronous [Fig. 1(*c*)]. As a consequence, binding of Ba^{2+} to the nitrogen lone pairs is diminished [see ^{13}C-shift of N-CH_2, Fig. 1(*c*)] and interaction of the Ba^{2+} with the redox centre is becoming now mostly governed by through-space. Since through-space interaction is weaker than through-bond interaction,[8] a drop in the redox potential at the Fe-centre is expected although the number of complexed ions increases when going to higher Ba^{2+}-concentrations. The partial liberation of the nitrogen lone pairs from binding to Ba^{2+} should now allow better overlap with the metal orbitals at the platinum electrode, thus an increase of the heterogeneous electron transfer rate is certainly reasonable.

For financial support we thank the Land Baden-Württemberg (electroactive systems for sensor applications), the Degussa and the Fonds der Chemischen Industrie.

Received, 31st October 1994; Com. 4/06639A

Footnotes

† Satisfactory C, H, N analyses were obtained for all iron(II) complexes.

‡ ΔE_p separation of anodic and cathodic peak potential.

§ The charge to radius values for K^+ and Ba^{2+} are 0.72×10^{-2} and 1.48×10^{-2} A s pm^{-1}, respectively.

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