Selective electrochemical recognition of mercury in water by a redox-functionalised aza-oxa crown derivative

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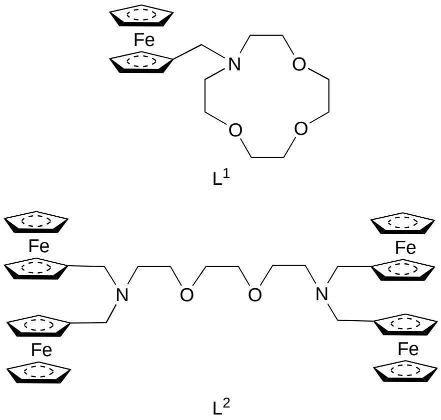
The ability of the new cyclic aza-oxa redox-active receptor *N*-ferrocenylmethyl-1,4,7-trioxa-10-azacyclododecane to selectively and electrochemically recognize Hg^{2+} in water over other commonly water-present metal ions is reported.

The design and synthesis of promising new materials from supramolecular chemistry for the development of novel chemical sensors is a field of current interest. Of special interest are novel functionalised molecules which are able to change an easily measurable physical property by coordination with a target substrate. Among these new molecules are redox-functionalised receptors able to display a shift of the redox potential upon addition of particular substrates.[1] We have recently been involved in the synthesis of electroactive water soluble receptors for the electrochemical recognition of toxic heavy metal cations. A combination of well known molecular properties and suitable redox groups could prove to be a good method to strategically design new molecules for the selective electrochemical recognition of target substrates. The design strategy was inspired by two well known properties; (*i*) macrocyclic receptors compared to acyclic structures generally provide more selective complexation, and (*ii*) the presence of central oxygen donors in macrocycles has been used to control the selectivity for large metal ions over small ones.[2,3] Taking these two principles into account the aza-oxa crown derivative 1,4,7-trioxa-10-azacyclododecane ([12]-aneNO_3),[4] which has been reported to display higher stability constants with mercury than with other common metal ions, was chosen and functionalised with ferrocenyl groups. Synthesis of L^1 was carried out by reaction of [12]-aneNO_3 with (ferrocenylmethyl)-trimethylammonium iodide in acetonitrile (Scheme 1).



Scheme 1

L^1 is an oil but can be obtained as a solid by adding $[NH_4][PF_6]$ to a solution of L^1 in ethanol and further addition of water to give $[HL^1][PF_6]$. Crystals‡ were obtained by slow diffusion of hexane into dichloromethane solutions of $[HL^1][PF_6]$. Fig. 1 shows the molecular structure of the $[HL^1]^+$ cation. The protonation constants of the free ligand and the stability constants for the formation of the Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} complexes of L^1 have been determined using potentiometric methods (25 °C, 0.1 mol dm^{-3} $KClO_4$; titration was carried out with KOH from previously acidified solutions with $HClO_4$ of L^1 and the corresponding metal ion).[6] Stability constants are gathered in Table 1. The formation of the $[ML^1(OH)]^+$ and $[ML^1(OH)_2]$ complexes has been observed for all the metal ions. Additionally, for Pb^{2+} and Hg^{2+}, $[ML^1]^{2+}$ species have also been found to exist. Functionalisation with the ferrocenyl group does not basically appear to modify the coordination behaviour of the cyclic oxa-aza cavity. Fig. 2 displays the distribution diagrams of the L^1–H^+–Cu^{2+} and L^1–H^+–Hg^{2+} systems. Hg^{2+} shows a quite different diagram and, when the $[HgL^1]^{2+}$ complex is predominant (near pH 5), there is not interaction between the receptor and Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions. This can be explained taking into account

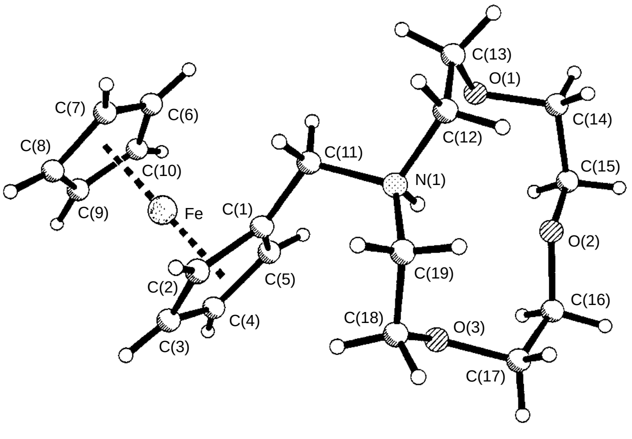


Fig. 1 Molecular structure of the $[HL^1]^+$ cation

Table 1 Stability constants (log *K*) for the formation of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} complexes of L^1 in H_2O at 25 °C in 0.1 mol dm^{-3} $KClO_4$[a]

	M				
Reaction	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
$M^{2+} + L^1 \rightleftharpoons [ML^1]^{2+}$	—	—	—	5.29(5)[b]	10.03(4)
$M^{2+} + L^1 + H_2O \rightleftharpoons [ML^1(OH)]^+ + H^+$	−0.72(2)	−3.49(3)	−6.19(2)	−3.47(7)	3.0(1)
$M^{2+} + L^1 + 2H_2O \rightleftharpoons [ML^1(OH)_2] + 2H^+$	−10.10(4)	−13.10(4)	−16.52(2)	−13.23(6)	−4.08(7)

[a] The titration curves were merged and treated simultaneously to give the stability constants: L^1–H^+–Hg^{2+}, three titration curves, pH 3–8; L^1–H^+–M^{2+} (M = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}), three titration cures, pH 3–9. [b] Values in parentheses are standard deviations on the last significant figure.

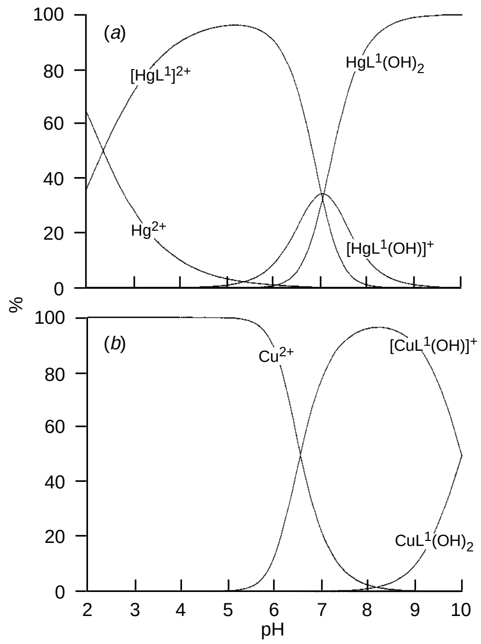


Fig. 2 Distribution diagram for the systems (*a*) L^1–H^+–Hg^{2+} and (*b*) L^1–H^+–Cu^{2+}

the larger affinity of Hg^{2+} for L^1, which is able to produce the reaction $Hg^{2+} + HL^{1+} \rightleftharpoons [HgL^1]^{2+} + H^+$ at a lower pH value than the remaining metal ions. To determine if the ferrocenyl group is able to amplify the selective mercury-binding behaviour found at molecular level into a macroscopic signal using electrochemical methods, the oxidation potential of the free receptor and the oxidation potential of L^1–M^{2+} systems ($M = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}$) has been monitored as a function of the pH in water. $E_{1/2}$ of the free receptor is pH-dependent. $E_{1/2}$ is *ca.* 175 mV at pH = 10. When the pH decreases there is an anodic shift until pH = 8 ($E_{1/2}$ = 375). In the pH range 8–3 the potential remains constant with a total shift between basic and acid pH of near 200 mV. Fig. 3 shows $\Delta E_{1/2}$ found in the presence of metal ions [$M = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}$; $\Delta E_{1/2}$ is defined for a particular pH as $E_{1/2}(L^1\text{–}H^+\text{–}M^{2+}) - E_{1/2}(L^1\text{–}H^+)$, studies have been carried out using 1:1 metal-to-ligand molar ratios; typical metal concentrations were $3\text{–}4 \times 10^{-4}$ mol dm^{-3}]. It can be observed that there is a selective electrochemical recognition of Hg^{2+} over other common typically water-present metal ions as was predicted from the potentiometric results. At pH 6 there is no interaction between L^1 and Cu^{2+}, Zn^{2+}, Cd^{2+} or Pb^{2+}, and the addition of these metal ions (*ca.* 3×10^{-4} mol dm^{-3}) to solutions of L^1 and Hg^{2+} ([Hg^{2+}] *ca.* 3×10^{-4} mol dm^{-3}) does not shift $E_{1/2}$. Additionaly L^1–M^{2+}–H^+ curves in Fig. 3 are transformed into the L^1–Hg^{2+}–H^+ curve by adding equimolecular amounts of mercury to L^1–M^{2+} solutions ($M^{2+} = Cu^{2+}, Zn^{2+}, Cd^{2+}$ or Pb^{2+}), indicating that Hg^{2+} is able to displace other metal ions in pre-formed $[ML^1]^{2+}$ complexes. L^1 behaves as a selective sensing molecule for Hg^{2+}.

To study the role played by the cyclic nature of L^1 similar experiments have been carried out using L^2 as receptor, which has been isolated after condensation of 2,2′-(ethylenedioxy)-bis(ethylamine) and (ferrocenylmethyl)trimethylammonium iodide. Electrochemical data showed, in contrast with L^1, that the values of $E_{1/2}$ *vs.* pH found for the free receptor and $E_{1/2}$ *vs.* pH obtained in the presence of metal ions ($M^{2+} = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}$ and Hg^{2+}; 1:1 metal-to-ligand molar ratios) were the same within the experimental error, pointing out the importance of the molecular architecture in L^1.

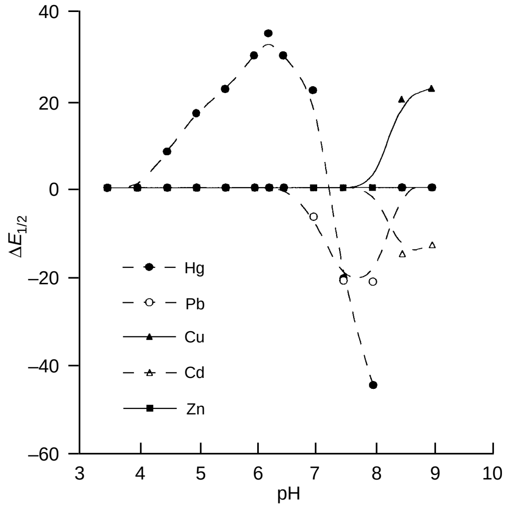


Fig. 3 Plot of $\Delta E_{1/2}$ *vs.* pH as a function of the pH for L^1–H^+–M^{2+} ($M^{2+} = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}$ and Hg^{2+})

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Notes and References

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‡ $C_{19}H_{28}F_6FeNO_3P$, M = 512.24, monoclinic, space group $P2_1$, a = 8.049(3), b = 10.353(4), c = 13.905(6) Å, β = 104.24(3)°, U = 1123.2(7) Å^3, Z = 2, D_c = 1.54 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, T = 293(2) K, μ(Mo-Kα) = 8.12 cm^{-1}. A well shaped crystal with approximate dimensions 0.15 × 0.15 × 0.25 mm was mounted on a Siemens P4 single-crystal diffractometer. A total of 2925 independent reflections were collected (R_{int} = 0.021) ($4.9 \leqslant 2\theta \leqslant 45.1°$). Lorentz and polarization corrections were applied and absorption was corrected from ψ-scans. The structure was solved by direct methods and refined by full-matrix least-squares analysis on F^2 (SHELXTL).[5] The refinement converged at R_1 = 0.0524 [$F > 4\sigma(F)$] and wR_2 0.1500 (all data). Largest peak and hole in the final difference map = +0.42, −0.20 e Å^{-3}. CCDC 182/785.

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