Ferrocenyldimethyl-[2.2]-cryptand: Solid State Structure of the External Hydrate and Alkali and Alkaline-earth-dependent Electrochemical Behaviour

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1,1′-(1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-diyldimethyl)ferrocene, ferrocenyldimethyl-[2.2]-cryptand **1**, binds water on its external face rather than internally and exhibits electrochemical behaviour that is strongly dependent on alkali and alkaline earth metal cations.

We report the electrochemical behaviour of 1,1′-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-diyldimethyl)ferrocene, ferrocenyldimethyl-[2.2]-cryptand, **1**, a redox-active ionophore[1] whose redox properties depend on the ferrocenyl nucleus.[2] The cryptand binds water on the external, macrocyclic portion of the molecule, and shows alkali and alkaline-earth-dependent electrochemistry in contrast to the behaviour of previously studied systems in this family.

Compound **1** was reported by Oepen and Vögtle[3] to be an oil but detailed spectral data were lacking. We obtained **1** as its crystalline hydrate, m.p. 101–104 °C, by using Hall's procedure[4] for the amide and then reducing 1,1′-(1,4,10,13-

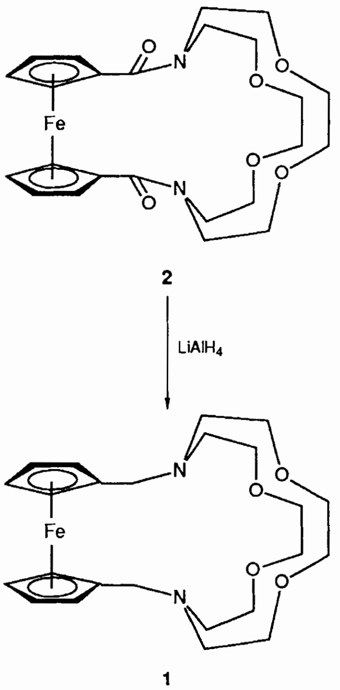
Table 1 Electrochemical data for **1** in the absence and in the presence of cations

Cation	Equiv.	Redox potential[a] $E_f°$	$E_c°$	$\Delta E°$	K/K_+[b]
None	0	0.216	—	—	—
Li^+	0.5	0.210	—	—	—
Na^+	0.5	0.214	0.402	0.188	1.5×10^3
K^+	0.5	0.224	0.348	0.124	1.2×10^2
Ca^{2+}	0.5	0.214	0.488[c]	0.274	4.3×10^4

[a] $E_f°$ and $E_c°$ are the redox potentials of the free ligand and the specified metal ion complex, respectively, and are given in V *vs.* standard sodium calomel electrode (SSCE). $\Delta E°$ is the difference between these two values. [b] K and K_+ stand for the binding constants of the reduced and oxidized forms of the ligand, respectively. The ratio K/K_+ was calculated by using the expression $K/K_+ = \exp\{F(E_c° - E_f°)/RT\}$. [c] This redox couple showed a substantial degree of electrochemical irreversibility.

tetraoxa-7,16-diazacyclooctadecane-7,16-diyldicarbonyl)ferrocene, **2**, using $LiAlH_4$ rather than B_2H_6 used by Vögtle (Scheme 1).†

The crystal structure (Fig. 1) of **1**·H_2O,‡ contrasts sharply with that reported **2**·$(H_2O)_2$ in that in the former two hydrogen bonds hold a single water molecule to the external surface of the diaza-18-crown-6 subunit whereas two water molecules are present in the structure of **2**.[5] In the latter, one water is coordinated to the carbonyl group and the other appears to fill a molecular void outside the ring. Even though the macrocyclic ring of **1** does not exhibit high symmetry in the solid state, it is more planar than the macrocyclic portion of **2**, and the macroring is more open since the Fc–CH_2 links of **1** are not required by conjugation to be coplanar as are the amide links of the former. The average distances observed in the structure of **1**·H_2O are: Fe–C, 2.049(6) C–C(C_5H_5), 1.425(8); H_w–O_w, 0.88(4), H_w–$O_{macroring}$, 2.06(6); C–N (macroring), 1.469(4); C–N (Fe–C–N), 1.475(12); C–O, 1.419(8); C–C (O–C–C–O), 1.482(8); C–C (O–C–C–N), 1.504(3); C–C (Fc–C), 1.502(4); and interring, 3.303 Å. The N · · · N distance in **1**·H_2O of 5.5, compared to 5.8 Å in the extended (C_{2h}) conformation of the parent macrocycle,[6] 4,13-diaza-18-crown-6 and 5.2 Å in **2**, reflects its intermediate rigidity. The difference in flexibility between compounds **1** and **2** is likewise reflected in the ^{13}C NMR spectra. Seven peaks are observed for **1**·H_2O whereas 11 are reported for **2** under comparable conditions.[4]



Scheme 1

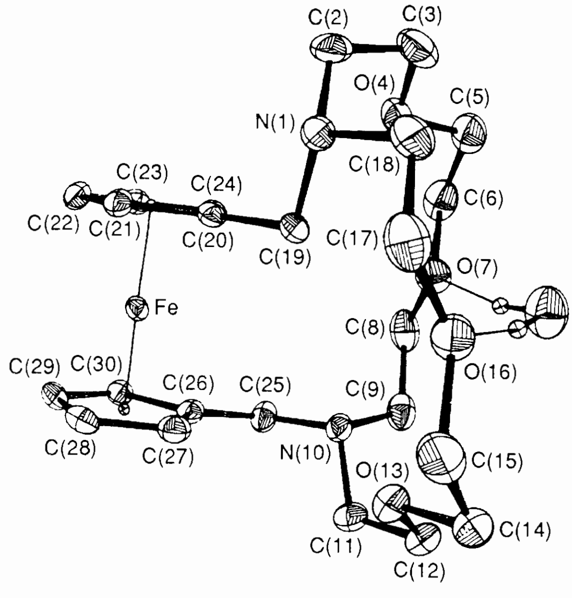


Fig. 1 The X-ray crystal structure of **1**·H_2O. (*a*) View perpendicular to the macrocycle cavity. (*b*) Side view.

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† To **2** (1.0 g 2.0 mmol) in CH_2Cl_2 (42 ml) containing anhydrous tetrahydrofuran (8 ml) under N_2 at ambient temperature was added excess $LiAlH_4$ (250 mg, 6.6 mmol) and the reaction was stirred for 30 min. The mixture was diluted with CH_2Cl_2 (50 ml) and quenched with Na^+K^+ tartrate (saturated aqueous solution, 50 ml), the organic phase was separated and washed with deionized water (3 × 50 ml), dried over $MgSO_4$, the solvent removed *in vacuo*, and the residue chromatographed over deactivated alumina (*ca.* 150 mesh, deactivated with H_2O, 3% by weight). The product eluted with 1% MeOH–CH_2Cl_2 followed by crystallization from diethyl ether–hexane to afford **1**·H_2O (0.584 g, 56%) as yellow-orange crystals, m.p. 101–104 °C. ^{13}C NMR ($CDCl_3$) δ 87.103, 70.583, 69.811, 69.680, 67.014, 54.056 and 53.364. ^1H NMR ($CDCl_3$) δ 4.26 (s, 4H), 4.05 (s, 4H), 3.80 (m, 4H), 3.67 (m, 16H), 2.80 (m, 4H) and 2.66 (m, 4H). DCI MS *m/z* (relative intensity) 474 (< 1,M + 2H$^+$), 473 (1,M + H$^+$), 472 (< 1, M$^+$), 263 (60), 214 (10), 132 (20). IR (KBr) ν/cm^{-1} 3400s, 2820s, 1435m, 1350m, 1270s, 1100s and 800m. Satisfactory microanalytical data were obtained.

‡ Crystals of **1**·H_2O suitable for X-ray analysis were grown by slow evaporation in a Et_2O–hexane mixture to afford yellow-orange crystals. The analysis was performed on a Enraf-Nonius CAD-4F diffractometer using a graphite monochromator, capillary mounted, radiation Mo-Kα. The crystal was plate-shaped of approximately 0.11 × 0.62 × 0.93 mm monoclinic, space group $P2_1/n_1$ $a = 9.932(2)$, $b = 11.195(1)$, $c = 22.249(4)$ Å, $V = 2429$ Å^3, $\beta = 100.97(2)°$, λ (Mo-Kα) = 0.71069 Å, $Z = 4$, $D_c = 1346$ g cm^{-3}, total number of reflections and unique reflections 4853 and 4579, respectively, $R = 0.037$, $R_w = 0.041$. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to the ferrocenyldimethyl-[2.2]-cryptand were placed at calculated positions and were allowed to ride on the bonded carbon atoms. The two hydrogen atoms of the water molecule were located on a difference Fourier map and were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centres. See Notice to Authors, Issue No. 1.

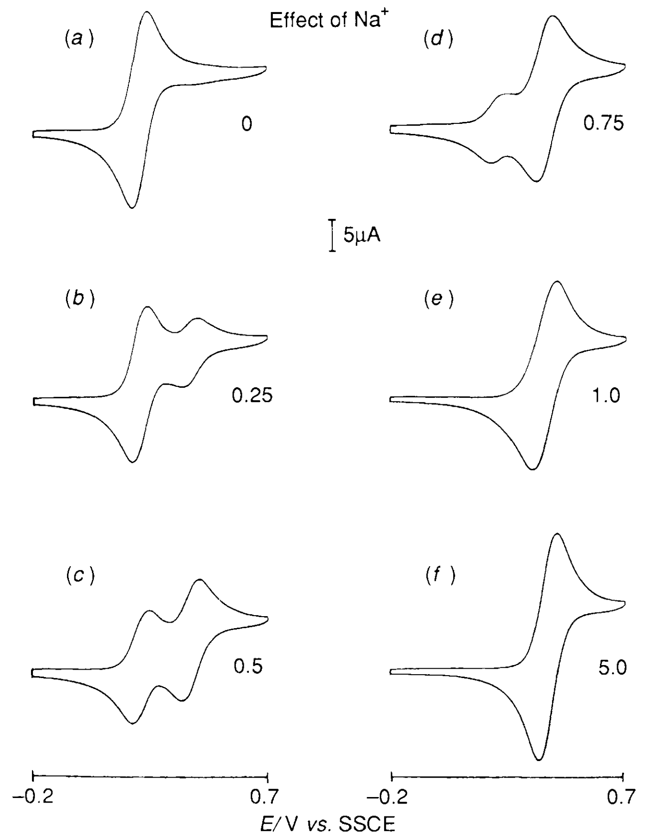

Fig. 2 Cyclic voltammetry on a glassy carbon electrode of **1** (1.0 mmol dm^{-3}) in MeCN–TBA$^+$PF$_6^-$ (0.1 mol dm^{-3}). Scan rate = 50 mV s^{-1}. (*a*) No Na$^+$. (*b*) 0.25 equiv. Na$^+$. (*c*) 0.50 equiv. Na$^+$. (*d*) 0.75 equiv. Na$^+$. (*e*) 1.0 equiv. Na$^+$. (*f*) 3.0 equiv. Na$^+$.

Cyclic voltammetry of **1**·H$_2$O in MeCN–TBA$^+$PF$_6^-$ (0.1 mol dm^{-3}; TBA = tetrabutylammonium) showed the expected reversible oxidation of ferrocene [Fig. 2(*a*)]. In the presence of 0.25 equiv. of NaClO$_4$, a second redox couple appeared at more positive potentials [Fig. 2(*b*)]. This new redox process corresponds to the reversible oxidation of the complex **1**·Na$^+$. As the concentration of Na$^+$ in the solution increased, the peak currents of the new redox couple also increased at the expense of the currents observed for the original **1**/**1**$^+$ couple which disappears in the presence of 1.0 equiv. of Na$^+$ cation (see Fig. 2). Since the oxidation of the Na$^+$ complex takes place at more positive potentials than the oxidation of the free ligand, we conclude that the ferricinium (oxidized) form of the complex is destabilized by repulsive electrostatic interactions with the ring-bound cation. This also means that **1** is acting as a redox-switchable ligand because its oxidized form, **1**$^+$, has a lower affinity for Na$^+$ than does **1**. However, **1**$^+$ still exhibits some affinity for Na$^+$ as evidenced by the complete reversibility of the redox couple corresponding to complex. This shows that the neutral macrocycle has rather a high Na$^+$ binding constant.

The binding ratio for Na$^+$ by **1**/**1**$^+$, *i.e.* K/K_+, can be calculated from the half-wave potentials of both redox couples. These ratios and the half-wave potentials observed in the presence of Li$^+$, Na$^+$, K$^+$ and Ca^{2+} are collected in Table 1. The difference between the half-wave potentials of the free ligand and the complex increases in the order K$^+$ < Na$^+$ < Ca^{2+}, as expected from the increasing charge-to-size ratios of these cations. Lithium cation has only a small effect on the voltammetric behaviour of **1** and its presence (at the concentrations surveyed) does not result in new redox couples. This is probably due to poor binding of Li$^+$ to the neutral macrocycle.

Compound **1** is the first ferrocene-based macrocycle that shows electrochemical behaviour sensitive to the presence of alkali metal cations in a solvent as polar as MeCN. Previous reports of ferrocene-based ionophores have demonstrated electrochemical changes caused either by lithium cation[2k] or divalent or trivalent cations[2l] which obviously exert much stronger electrostatic effects on the system. To our knowledge, only Saji has reported Na$^+$ effects on the electrochemistry of a ferrocenyl crown ether system,[2a] but those experiments were conducted in the far less polar solvent CH$_2$Cl$_2$, a solvent that competes weakly with the macrocyclic donor system. The Na$^+$- and K$^+$-dependent electrochemical behaviour of **1** in MeCN is due to a combination of nitrogen atom basicity and greater conformational mobility compared to **2**. We also note that $\Delta E°$ for **1**·Ca^{2+} (274 mV) is substantially greater than the corresponding value for **2** (155 mV).[2l] Thus, **1** appears to be the most versatile redox-switchable, ferrocene-derived ionophore yet studied.

We warmly thank the National Institutes of Health (GM 36262 to G. W. G.) and the National Science Foundation (CHE-900053 to A. K.) for grants that supported this work.

Received, 6th August 1990; Com. 0/03620J

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