1,2-FDTA: A Ferrocene-Based Redox-Active EDTA Analogue with a High Ca^{2+}/Mg^{2+} and Ca^{2+}/Sr^{2+} Selectivity in Aqueous Solution

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1,2-Ferrocenemethylenediyldiamino tetraacetate (1,2-FDTA) is a redox-active relative of EDTA and was synthesized in the reaction of 1,2-bis(chloromethyl)ferrocene with iminodiacetate methyl ester followed by cleavage of the ester with methanolic KOH. Potentiometric determination of the stability constants of the complexes of 1,2-FDTA with the alkaline earth metal ions showed this ligand to display a higher Ca^{2+}/Mg^{2+} and Ca^{2+}/Sr^{2+} selectivity (Ca^{2+} log $K = 6.56$, Mg^{2+} log $K = 4.65$, Sr^{2+} log $K = 3.32$) than EDTA itself. The redox potential of 1,2-FDTA-Ca^{2+} determined in aqueous solution by cyclic voltammetry was found to be anodically shifted by +50 mV with respect to that of the calcium free complex. Consequently the redox-inactive calcium can be determined electrochemically in aqueous solution with a high selectivity with respect to the other alkaline earth metal ions.

EDTA (ethylenediamino tetraacetate) has found widespread use in analytical chemistry for the determination of metals, since it forms very stable complexes with a large number of metal ions.[1] It is well suited for the complexation of alkaline earth metal ions and thus very useful for the quantitative determination of calcium, because it displays a remarkable Ca^{2+}/Mg^{2+} selectivity.[2] Ferrocene continues to be among the most prominent organometallic compounds and displays numerous interesting properties among which its ability to undergo reversible one-electron transfer processes is one of the most important.[3] The combination of ferrocenes with macrocyclic polyethers[4] or chelating ligands[5] has resulted in a number of attractive compounds, which have been used as redox-receptors for cations and anions,[6] redox-switched crown ethers[7] or as hydrogenase models[8] since the redox potential of the metallocene is influenced reversibly by coordination of metal cations by the appended macrocyclic or chelating ligand.

With a view to the development of amperometric sensor devices for alkaline earth metal ions[9] it therefore seemed very attractive to synthesize an electrochemically active ligand, which has the same coordination characteristics as EDTA.

We have recently described the synthesis of a 1,1′-substituted ferrocene which carries one iminodiacetate group on each cyclopentadienyl ring and determined the stability constants of the complexes with alkaline earth metal ions.[10] The complexes with Mg^{2+} and Ca^{2+} are reasonably strong in water [log $K(Mg^{2+}) = 4.63$, log $K(Ca^{2+}) = 4.97$] but a selectivity for any of the group II metal ions was not observed. We therefore anticipated that attaching the functional groups of EDTA at the 1,2-positions of one cyclopentadienyl ring of ferrocene would render the resulting complexon much more similar to EDTA than the highly flexible 1,1′-substituted ferrocene species.

In this paper the synthesis of 1,2-ferrocenemethylenediyldiamino tetraacetate (1,2-FDTA), the electrochemical behavior and the potentiometric determinations of the stability constants of the complexes of alkaline earth metal ions with this ligand will be described and it will be shown that the complexation characteristics of 1,2-FDTA are closely related to those of EDTA.

Results and Discussion

Syntheses of the Ferrocenylimino Diacetates

The reaction of chloromethylferrocene with $HN(CH_2COOMe)_2$ in the presence of a base results in the formation of methyl ferrocenylimino diacetate in a yield of 64%. The methyl ester was hydrolyzed to the ferrocenylimino diacetate by refluxing a methanolic KOH solution for 4 h. A yellow precipitate consisting of the dipotassium salt of ferrocenylimino diacetate (FIA) could be isolated and was used for all following investigations (Scheme 1).

For the synthesis of 1,2-FDTA, 1,2-di(hydroxymethyl)ferrocene was treated with PCl_3 resulting in the formation of the previously unknown 1,2-bis(chloromethyl)ferrocene. This highly reactive compound was treated with two equivalents of $HN(CH_2COOMe)_2$ to yield 1,2-$[CH_2N(CH_2COOMe)_2]_2$-ferrocene in a 44% yield. The ester cleavage was again performed in methanolic KOH to generate the respective tetraacetate [1,2-FDTA-(4 K^+)] in 71% yield, which was used for all further investigations (Scheme 1), since treatment of this salt with HCl did not lead to the free ferrocenyl diiminotetraacetic acid but only resulted in decomposition of the ferrocene instead.[11] The tetraacetate 1,1′-FDTA was available from previous investigations (Scheme 1).[10]

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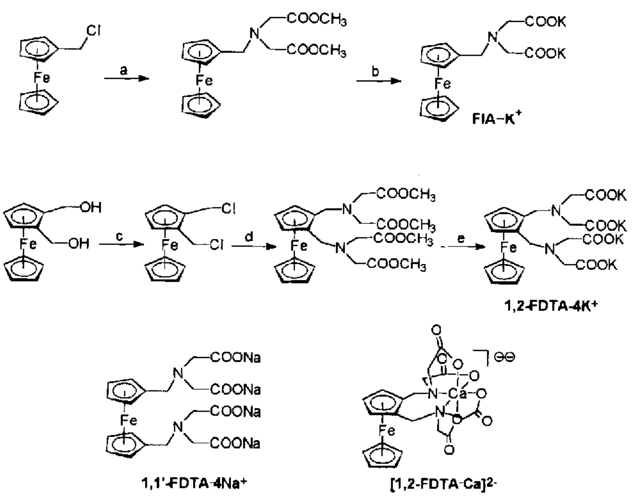
Scheme 1. Synthesis and ferrocene-based EDTA relatives and proposed structure of 1,2-FDTA-Ca; reaction and conditions: a) iminodiacetic acid methyl ester, Et_3N in Et_2O; b) KOH/MeOH, reflux; c) PCl_3 in THF; d) iminodiacetic acid methyl ester, Et_3N in Et_2O; e) KOH/MeOH, reflux



Determination of the Stability Constants

The stability constants of the complexes of the alkaline earth metal ions Mg^{2+}, Ca^{2+}, and Sr^{2+} with FIA and 1,2-FDTA were determined by potentiometric titrations and the evaluation of the data was conducted with the program TITFIT.[12]

The pK_2 value of FIA thus calculated is 9.58 and is comparable to that of $(HOOCCH_2)_2N-[CH_2]_5-N(CH_2COOH)_2$ in which the two nitrogen centers are virtually independent from each other (Table 1). The complexes of Mg^{2+}, Ca^{2+}, and Sr^{2+} with FIA are weak and the stability constants are in the same range as observed for the complexes of iminodiacetate or *N*-benzyliminodiacetate (Table 3). For calcium and strontium the 1:1 complexes are preferentially formed, whereas in the magnesium complex of FIA a MgL_2 species is important (log $\beta_2 = 7.16$). In conclusion the complexes of FIA are equally weak for the three metal ions investigated and are not suitable as redox-active equivalents of EDTA.

In the case of 1,2-FDTA the pK_3 and pK_4 values were determined to be 7.73 and 8.90. While the pK_3 value is in the range found for other EDTA derivatives with closely spaced nitrogen atoms (Table 1), the pK_4 value is surprisingly low, since in all other EDTA relatives the first protonation occurs at close to pK_4 ca. 10.4. An explanation for this low pK_4 value is not close at hand. In this respect one should, however, remember that due to the 1,2-substitution pattern at the cyclopentadienyl ring two orientations of the nitrogen atoms with respect to the ferrocene can be distinguished, which lead to an unusual stereochemistry in this molecule.

Table 1. pK_3 and pK_4 values of $(HOOCCH_2)_2N-(CH_2)_n-N(CH_2COOH)_2$ and 1,1'-FDTA and 1,2-FDTA (*n* is the number of CH_2 groups separating the iminodiacetate groups)

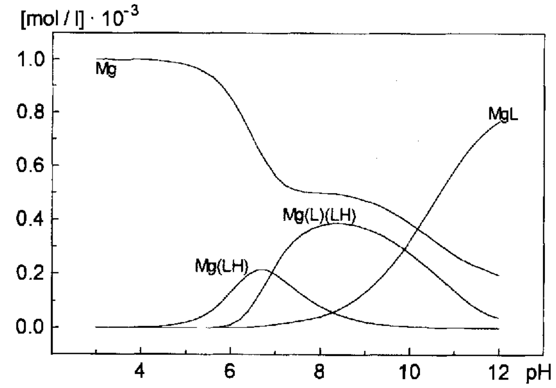
n =	2	3	4	5	1,1'-FDTA	1,2-FDTA
pK_3	6.16	7.90	9.07	9.50	9.18	7.73
pK_4	10.26	10.27	10.45	10.58	10.27	8.90

The stabilities of the complexes of 1,2-FDTA with Mg^{2+}, Ca^{2+}, and Sr^{2+} were determined by potentiometric titrations and the distribution curves for the concentrations of the different species, depending on the pH value, are depicted in Scheme 2 (1,2-FDTA-Mg^{2+}) and Scheme 3 (1,2-FDTA-Ca^{2+}). Prior to looking at stability constants derived from these data it can be easily seen in these schemes upon looking at the concentrations of free Ca^{2+} and Mg^{2+} that the former metal forms much more stable complexes than Mg^{2+} with 1,2-FDTA. The calculated overall stability constants β of the Mg^{2+}, Ca^{2+}, and Sr^{2+} complexes of 1,2-FDTA are listed in Table 2, while a listing of the stabilities of the different 1:1 complexes of these metal ions with 1,2-FDTA and related ligands is found in Table 3. Upon comparing the 1:1-magnesium complexes of 1,1'-FDTA-Mg^{2+} and 1,2-FDTA-Mg^{2+} virtually the same stabilities (log β_1 = 4.63 vs. 4.65) were found. Very much in contrast the 1:1-calcium complex of 1,2-FDTA is much more stable than that of 1,1'-FDTA with the same metal ion. More significantly so 1,2-FDTA-Ca^{2+} is by almost two orders of magnitudes more stable than the complex of Mg^{2+} with the same ligand, hence documenting a very pronounced selectivity of Ca^{2+} over Mg^{2+} complexation. The difference between the two log*K* values amounts to $\Delta\log K = 1.91$ which is even slightly larger than the Ca^{2+}/Mg^{2+}-selectivity displayed by EDTA itself ($\Delta\log K = 1.75$). The strontium complex of 1,2-FDTA is much less stable than those of calcium and magnesium resulting in a Ca^{2+}/Sr^{2+} selectivity of $\Delta\log K = 3.24$, which is much better than the Ca^{2+}/Sr^{2+} selectivity displayed by EDTA ($\Delta\log K = 2.16$). However, in general the stabilities of the complexes of 1,2-FDTA are much lower than those of EDTA, but nonetheless the calcium complex of 1,2-FDTA is almost as stable as that of the tetraacetate in which three CH_2 units separate the two iminodiacetate groups (Table 3).

Cyclic Voltammetry

The fundamental difference between the ferrocene based ligands described here and EDTA is the ability of the for-

Scheme 2. Distribution curves of the 1,2-FDTA-Mg^{2+} complexes in a solution containing 1,2-FDTA ($0.904 \cdot 10^{-3}$ mol/l) and Mg^{2+} ($1.000 \cdot 10^{-3}$ mol/l)



Scheme 3. Distribution curves of the 1,2-FDTA-Ca^{2+} complexes in a solution containing 1,2-FDTA ($0.904 \cdot 10^{-3}$ mol/l) and Ca^{2+} ($1.018 \cdot 10^{-3}$ mol/l)

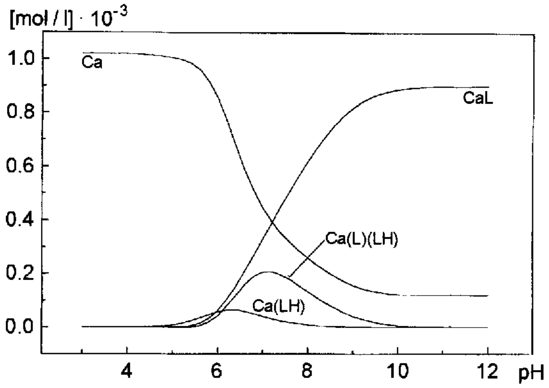


Table 2. Stability constants for the complexes of 1,2-FDTA with Ca^{2+}, Mg^{2+}, and Sr^{2+}

species	log β(Mg^{2+})	log β(Ca^{2+})	log β(Sr^{2+})
ML	4.65	6.56	3.32
M(LH)	12.92	12.63	12.36
M(L)(LH)	19.36	20.06	17.59

Table 3. Stability constants of the 1:1 complexes of 1,2-FDTA, 1,1'-FDTA, EDTA, and related complexons with alkaline earth metal cations

ligand	Mg^{2+}	Ca^{2-}	Sr^{2+}	Ba^{2+}	reference
iminodiacetate	2.94	2.59	2.23	1.67	[18]
N-benzyliminodiacetate	2.63	3.13	–	–	[19]
FIA	3.17	3.55	2.94	–	this work
EDTA	8.69	10.44	8.28	8.0	[18]
$[CH_2]_3[N(CH_2COOH)_2]_2$	6.02	7.12	5.18	4.24	[20]
1,1'-FDTA	4.63	4.97	3.91	3.06	[10]
1,2-FDTA	4.65	6.56	3.32	–	this work

Table 4. Redox potentials $E_{1/2}$ of FIA, 1,2-FDTA, and 1,1'-FDTA and their alkaline earth metal complexes in aqueous solution at pH = 10; $\Delta E_{1/2}$ is the anodic shift of the redox potential upon addition of alkaline earth metal salts relative to the $E_{1/2}$ of the potassium complex of the respective ferrocene

ferrocene	$E_{1/2}$ [V]	$\Delta E_{1/2}$ [mv]
FIA-K^+	+0.20	–
FIA-Mg^{2+}	+0.22	+20
FIA-Ca^{2+}	+0.25	+50
FIA-Sr^{2+}	+0.23	+30
FIA-Ba^{2+}	+0.22	+20
1,2-FDTA-K^+	+0.26	–
1,2-FDTA-Mg^{2+}	+0.36	+100
1,2-FDTA-Ca^{2+}	+0.31	+50
1,2-FDTA-Sr^{2+}	+0.28	+20
1,1'-FDTA-K^+	+0.24	–
1,1'-FDTA-Mg^{2+}	+0.31	+70
1,1'-FDTA-Ca^{2+}	+0.32	+80

mer to undergo (reversible) one-electron redox processes, which adds a new dimension to this class of ligands, especially when the coordination chemistry of otherwise redox-inactive metal ions is investigated. Even though the possible redox potential window in water is fairly small due to oxidative or reductive cleavage of the solvent, the redox potentials of the ferrocenes studied here are easily accommodated in the allowed potential range, thereby presenting no problems for the electrochemical studies.

The redox potentials of the potassium salts of FIA ($E_{1/2}$ = +0.20 V), 1,2-FDTA ($E_{1/2}$ = +0.26 V) and 1,1'-FDTA ($E_{1/2}$ = +0.24 V) and those of their respective metal complexes were determined in water solution and are given in Table 4. Complexation of metal cations by these ligands leads to anodic shifts $\Delta E_{1/2}$ of the ferrocene redox potential, whose amount depends on the degree of electronic communication between the two metal centers.[13]

The redox potential shifts $\Delta E_{1/2}$ upon complexation of the dicationic metal ions are listed relative to the potentials of the respective potassium complexes. It is obvious from these data that the redox shifts $\Delta E_{1/2}$ of FIA group-II metal complexes are small regardless of the metal salt added. In the complexes of 1,2-FDTA and 1,1'-FDTA larger $\Delta E_{1/2}$ value s of up to +100 mV result from the complexation of metal ions, which can be easily monitored despite the typically much broader redox waves displayed in water solution. Noteworthy is the calcium induced +50 mV redox potential shift of 1,2-FDTA, which is smaller than the $\Delta E_{1/2}$ = +100 mV of Mg^{2+} but the strong preference of Ca^{2+} vs. Mg^{2+} complexation allows the easy detection of the heavier metal ion even in the presence of excess magnesium.

Conclusions

We have demonstrated that it is possible to synthesize an organometallic ferrocene-based relative of EDTA. The complexon (1,2-Ferrocenemethylenediyl)-Diamino Tetra-Acetate (1,2-FDTA) displays important characteristics of EDTA, which are a high selectivity for the complexation of Ca^{2+} vs. Mg^{2+} as well as a fairly high stability constant of the Ca^{2+} complex (log K = 6.56). In addition the appended redox-active ferrocene unit allows the highly selective electrochemical detection of an otherwise redox-inactive metal such as calcium even in the presence of excess magnesium or strontium, thus making this compound a potential amperometric sensor component.

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Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. – NMR spectra were recorded at 300 K with a Bruker AC200 F (^1H NMR: 200 MHz; ^{13}C NMR: 50 MHz). ^1H NMR was referenced to residual hydrogen in the deuterated solvents and ^{13}C NMR to the signals of the solvent: $CDCl_3$ (δ = 7.26, 77.0) or in D_2O with respect to TSP standard (δ = 0.00). – Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. – Infrared spectra of KBr tablets were recorded with a Bruker IFS 25 . – Cyclic voltammetry: The standard electrochemical instrumentation consisted of an Amel System 5000 potentiostat/galvanostat. Cyclic voltammogramms were recorded in demineralized water at ambient temperature using Amel software for a PC. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass, the counter electrode was a Pt wire, the potentials were referenced with an Ag/AgCl reference electrode. KCF_3SO_3 (0.1 M) was used as a supporting electrolyte. – Starting materials were commercially available or synthesized according to literature procedures: 1,2-bis(hydroxymethyl)ferrocene,[14] chloromethylferrocene,[15] $HN(CH_2COOMe)_2$.[16]

Potentiometry: Experimental conditions were as described previously.[17] Overall stability constant β_{mlh} (m = number of metal ions, l = number of ligand molecules, h = number of protons): β_{110}: M + L = ML; β_{111}: M + L + H = [M(LH)] ; β_{121}: M+ 2 L+ H = M(L)(LH). Stepwise stability constants K_{mlh}: K_{111}: M + LH = (MLH) , log K_{111} = log β_{111} − log β_{110}.

$$\beta_N = \prod_{n=1}^{N}$$

$$\sigma(ml) = \sqrt{\frac{\sum (ml_{exp} - ml_{calc})^2}{(n_m - n_{var})}}$$

σ(ml) determines the quality of the fit of the proposed species distribution for TITFIT, ml_{exp} and ml_{calc} = added or calculated volume of NaOH solution, n_m = number of titrant additions, n_{var} = number of variables in the model. For a summary of potentiometric data see Table 5. Even though we did not observe any clouding of the solution due to the precipitation of $Mg(OH)_2$ this could be possible at pH ≥ 10.

Table 5. Summary of selected potentiometric data

Measurement	Species	log β_{MLH}	σ (ML)	c_{ligand}, c_{metal} [10^{-3} mol/l]
FIA	011	9.58(4)	0.0028	1.005
FIA + Ca^{2+}	CaL	3.55(9)	0.0033	1.000
FIA + Mg^{2+}	MgL	3.17(14)	0.0034	1.019
	MgL_2	7.16(8)		
FIA + Sr^{2+}	SrL	2.94(14)	0.0030	1.000
1,2-FDTA	011	7.73(7)	0.0015	0.904
	012	8.90(2)		
1,2-FDTA + Ca^{2+}	CaL	6.56(8)	0.0025	1.018
	Ca(LH)	12.63(9)		
	Ca(L)(LH)	20.06(15)		
1,2-FDTA + Mg^{2+}	MgL	4.65(9)	0.0019	1.000
	Mg(LH)	12.92(9)		
	Mg(L)(LH)	19.36(15)		
1,2-FDTA + Sr^{2+}	SrL	3.32(14)1	0.0028	1.235
	Sr(LH)	2.36(10)1		
	Sr(L)(LH)	7.59(15)		

$Fc[CH_2N(CH_2COOMe)_2]$: To a solution of chloromethylferrocene (1.94 g, 8.2 mmol) in diethyl ether (30 ml) were added Et_3N (2 ml) and $HN(CH_2COOMe)_2$ (3.0 g, 18.6 mmol). After stirring for 12 h, the reaction mixture was filtered and the ethereal solution washed with aq. Na_2CO_3. The organic layer was separated, dried with $MgSO_4$ and the solvent evaporated. The remaining pale yellow oil was purified by chromatography (silica gel, cyclohexane/ethyl acetate = 10:1). Yield: 1.9 g (64%). – ^1H NMR (C_6D_6): δ = 3.28 (s, 6 H, OCH_3), 3.54 (s, 4 H, NCH_2), 3.80 (s, 2 H, $FcCH_2$), 3.92–4.14 (m, 9 H, FcH). – ^{13}C NMR (C_6D_6): δ = 50.78, 53.59, 53.76, 68.39, 70.26, 83.86, 171.23. – IR [ν(CO)]: $\tilde{\nu}$ = 1752, 1738 cm^{-1}.

$Fc[CH_2N(CH_2COOK)_2]$ (**FIA-2K$^+$**): $Fc[CH_2N(CH_2COOMe)_2]$ (0.95 g, 2.6 mmol) was dissolved in methanolic 2 N KOH (20 ml) and heated under reflux for 4 h, whereupon a yellow precipitate formed. This solid was centrifuged off, the liquid decanted and the precipate washed with methanol three times. Yield: 0.63 g (61%). – ^1H NMR (D_2O): δ = 3.10 (s, 2 H, $FcCH_2$), 3.68 (s, 4 H, CH_2COO^-), 4.23 (m, 7 H, FcH), 4.28 ("t", J = 1.7 Hz, 2 H, FcH). – ^{13}C NMR (D_2O): δ = 54.81, 60.04, 71.05, 71.58, 84.14, 182.06. – IR [ν(CO)]: $\tilde{\nu}$ = 1613, 1590 cm^{-1}.

1,2-$(CH_2Cl)_2$-Fc: To a solution of 1,2-$(CH_2OH)_2$-Fc (1.5 g, 6.1 mmol) and pyridine (2 ml) in THF (40 ml) was added freshly distilled PCl_3 (0.5 ml, 5.4 mmol), dissolved in THF (10 ml). After stirring for 3 h, the solution was filtered and the volatiles were removed from the filtrate. The remaining solid was recrystallized from petroleum ether. The yellow product decomposes at room temperature and should be stored at −20 °C. Yield: 1.6 g (90%). – ^1H NMR (C_6D_6): δ = 3.75 (s, 5 H, FcH), 3.78 (t, J = 3.8 Hz, 1 H, FcH), 3.94 (d, J = 3.7 Hz, 2 H, FcH), 3.97 (d, J = 12 Hz, CH_2Cl), 4.07 (d, J = 12 Hz, CH_2Cl). – ^{13}C NMR (C_6D_6): δ = 41.25, 68.29, 69.66, 70.28, 83.52.

1,2-$[CH_2N(CH_2COOMe)_2]_2$-Fc: To a solution of 1,2-$(CH_2Cl)_2$-Fc (1.6 g, 5.7 mmol) and Et_3N (3.0 ml) in ether (50 ml) was added $HN(CH_2COOMe)_2$ (2.0 g, 12.2 mmol). After stirring for 12 h, the reaction mixture was washed with aqueous Na_2CO_3. The ethereal layer was separated, dried with $MgSO_4$, filtered, and the solvent evaporated. The remaining brown oil was purified by chromatography (cyclohexane/ethyl acetate = 1:1). Yield: 1.3 g (44%). – ^1H NMR (C_6D_6): δ = 3.32 (s, 12 H, OCH_3), 3.68 (s, 8 H, NCH_2), 3.84 (m, 6 H, FcH), 3.86 (d, J = 12.6 Hz, 2 H, $FcCH_2$), 3.96 (d, J = 12.8 Hz, 2 H, $FcCH_2$), 4.16 (d, J = 2.4 Hz, 2 H, FcH). – ^{13}C NMR (C_6D_6): δ = 50.75, 52.10, 54.07, 67.11, 69.51, 71.08, 84.27, 171.59.

1,2-$[CH_2N(CH_2COOK)_2]_2$-Fc (**1,2-FDTA-4K$^+$**): 1,2-$[CH_2N(CH_2COOMe)_2]_2$-Fc (1.3 g, 2.4 mmol) was dissolved in methanolic 2 N KOH (20 ml) and heated under reflux for 4 h, whereupon a brown precipitate formed. This solid was centrifuged off, the liquid decanted and the precipitate washed with methanol three times. The residue was dissolved in water and freeze-dried. Yield: 1.2 g (71%). – ^1H NMR (D_2O): δ = 3.05–3.30 (m, 8 H, CH_2COO^-), 3.37 (d, J = 12.2 Hz, 2 H, $FcCH_2$), 3.84 (d, J = 12.3 Hz, 2 H, $FcCH_2$), 4.16 (s, 2 H, FcH), 4.29 (d, J = 2.0 Hz, 2 H, FcH). – ^{13}C NMR (D_2O): δ = 55.94, 61.4 (br.), 70.04, 72.17, 75.34, 85.37, 181.85 (br.). – $C_{20}H_{20}FeK_4N_2O_8$ (628.63): C 38.21, H 3.21, N 4.46; found: C 38.67, H 3.76.

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