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## Short Communication

# Ferrocene containing chelating ligands Part 2. Synthesis, characterization, electrochemical behaviour and crystal structure of 2-ferrocenylmethylamino-benzoic acid

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## Abstract

Ferrocenecarboxaldehyde reacts with 2-amino-benzoic acid in benzene to give the Schiff base derivative 2-ferrocenylmethylidenimino-benzoic acid $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}C_6H_4\text{–}COOH]$ (**1**). **1** is stable as a solid but easily hydrolyzes in solution. Selective hydrogenation of the imine group can be performed using $NaBH_4$ to obtain the parent amine $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH_2\text{–}NH\text{–}C_6H_4\text{–}COOH]$. (**2**). The molecular structure of **2** has been determined by single-crystal X-ray methods. It crystallizes in the space group $P2_1/c$, $a=11.077(9)$, $b=7.430(2)$, $c=19.194(9)$ Å, $\beta=111.02(4)°$, $V=1474(2)$ Å$^3$, $Z=4$. Refinement of the structure gave final $R$ factor of 0.038 ($R_w=0.035$) for 1106 unique reflections having $F_o^2>2.8\sigma(F_o^2)$. **2** is stable both in the solid state and solution, and a potential chelating N,O-donor ligand containing a ferrocenyl group. A one-electron oxidation process was found by cyclic voltammetry (0.1 M $NBu^n{}_4PF_6$, $CH_2Cl_2$) for **1** and **2** at 0.74 and 0.51 V, respectively.

## Introduction

Organometallic ligands containing one or more ferrocenyl groups and their coordination ability towards metal ions or other guest species have been a subject of great interest in recent years. The incorporation of ferrocene into an organic host structural framework with the aim of obtaining ferrocene-containing derivatives able to act as molecular or ion receptors [1, 2], the occurrence of ferrocene groups in close proximity to a host binding site [2, 3], their one-electron reversible redox-active behaviour [4, 5], and the possibility of using them as precursors for polynuclear metal complexes [1, 6], make ferrocene-containing molecules of considerable current interest in fields such as organometallic and coordination chemistry.

We have undertaken the incorporation of ferrocene into the skeleton of classical chelating N-donor or N,O-donor ligands able to coordinate metal ions in order to obtain polynuclear metal complexes containing an easily oxidizable redox active group. As a part of this work subject were report here the synthesis of 2-ferrocenylmethylidenimino-benzoic acid, $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH{=}N\text{–}C_6H_4\text{–}COOH]$ (**1**), and 2-ferrocenylmethylamino-benzoic acid, $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)\text{–}CH_2\text{–}NH\text{–}C_6H_4COOH]$ (**2**), as new potential ligands containing a ferrocenyl group. Their spectroscopic characterization and electrochemical behaviour are also reported, together with the crystal structure of **2**.

## Experimental

### *Materials*

Ferrocenecarboxaldehyde, 2-amino-benzoic acid and sodium borohydride were obtained from commercial sources and were used without further purification. The salt tetra-n-butylammonium hexafluorophosphate, ($NBu^n{}_4PF_6$), was recrystallized from ethanol solutions and dried at 80 °C under vacuum for 48 h. Tetrahydrofuran used was freshly distilled from sodium/benzophenone. Elemental analysis (C, H, N) was performed by the Servicio de Microanálisis Elemental de la Universidad Autónoma de Madrid (Spain).

### *Synthesis of 2-ferrocenylmethylidenimino-benzoic acid (1)*

274 mg of 2-amino-benzoic acid (2 mmol) and 428 mg of ferrocenecarboxaldehyde (2 mmol) were suspended in 50 ml of benzene, and the solution was refluxed under argon atmosphere for 3 h. The resulting solution was evaporated to dryness under reduced pressure and the crude oil was dissolved in 10 ml of dichloromethane. Addition of hexane gave a red solid which was filtered, washed with hexane and dried under

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vacuum (533 mg, 80% yield). *Anal.* Found: C, 64.11; H, 4.44; N, 4.47. Calc. for $C_{18}H_{15}NO_2Fe$: C, 64.89; H, 4.54; N, 4.20%. $^1H$ NMR ($CDCl_3$) spectrum (in ppm): 4.27 ($C_5H_5$, 5H, s), 4.70 ($C_5H_4$, 2H, s), 4.86 ($C_5H_4$, 2H, s), 6.67 ($C_6H_4$, 1H, t, $J=7$ Hz), 7.57 ($C_6H_4$, 1H, d, $J=8$ Hz), 7.94 ($C_6H_4$, 1H, t, $J=7$ Hz), 8.32 (CH, 1H, s), 8.68 ($C_6H_4$, 1H, d, $J=8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum (in ppm): 69.29 ($C_5H_4$), 69.68 ($C_5H_5$), 73.41 ($C_5H_4$), 76.62 ($C_5H_4$), 122.51 ($C_6H_4$), 126.48 ($C_6H_4$), 131.93 ($C_6H_4$), 133.69 ($C_6H_4$), 134.27 ($C_6H_4$), 146.73 (CH), 150.88 ($C_6H_4$), 167.89 (COOH). IR spectrum (KBr disk): 1660s, 1603s, 1579s, 1446m, 1388s, 1362m, 1229s, 1152m, 1098m, 1032m, 996m, 820m, 747s, 696m, 645m.

### *Synthesis of 2-ferrocenylmethylamino-benzoic acid (2)*

667 mg of **1** (2 mmol) were dissolved in 50 ml of freshly distilled tetrahydrofuran under argon atmosphere and 151 mg (4 mmol) of $NaBH_4$ were added. The mixture was stirred and refluxed for 90 min. Small amounts of water were added to the reaction mixture in order to eliminate the excess $NaBH_4$. The solution was evaporated under vacuum and water (20 ml) was added. Further addition of 10 ml of dichloromethane produced yellow organic phases which were separated using a separatory funnel. The extraction process was repeated three times. The dichloromethane solution was treated with anhydrous sodium sulfate, filtered and evaporated to reduce the volume to 5 ml. Addition of hexane gave a yellow crystalline solid which was filtered washed with hexane and dried under reduced pressure (502 mg, 75% yield). *Anal.* Found: C, 63.86; H, 5.00; N, 3.93. Calc. for $C_{18}H_{17}NO_2Fe$: C, 64.50; H, 5.11; N, 4.18%. $^1H$ NMR (dmso-$d^6$) spectrum (in ppm): 4.03 ($CH_2$, 2H, s), 4.15 ($C_5H_4$, 2H, br), 4.22 ($C_5H_5$, 5H, s), 4.24 ($C_5H_4$, 2H, br), 6.57 ($C_6H_4$, 1H, t, $J=8$ Hz), 6.80 ($C_6H_4$, 1H, d, $J=8$ Hz), 7.36 ($C_6H_4$, 1H, t, $J=8$ Hz), 7.81 ($C_6H_4$, 1H, d, $J=8$ Hz). $^{13}C\{^1H\}$ NMR (dmso-$d^6$) spectrum (in ppm): 41.29 ($CH_2$), 67.23 ($C_5H_4$), 67.44 ($C_5H_4$), 68.45 ($C_5H_5$), 85.87 ($C_5H_4$), 110.03 ($C_6H_4$), 111.30 ($C_6H_4$), 114.19 ($C_6H_4$), 131.59 ($C_6H_4$), 134.38 ($C_6H_4$), 150.52 ($C_6H_4$), 170.03 (COOH). IR spectrum (KBr disk): 3346s, 1651s, 1562s, 1502s, 1490m, 1445m, 1425s, 1389m, 1038m, 1239s, 1155m, 1092m, 1032w, 1018m, 994m, 800m, 746s, 644m.

### *Physical techniques*

IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer as KBr pellets. NMR spectra were measured on a Brucker AC-200 FT spectrometer operating at 300 K. $^1H$ NMR chemical shifts are reported in $\delta$ versus $Me_4Si$, $^{13}C\{^1H\}$ NMR (at 50.32 MHz) chemical shifts versus the $CDCl_3$ resonance ($^{13}C$, 77.00 ppm) and the dmso-$d^6$ ($^{13}C$, 39.50). Cyclic voltammograms were obtained with a programmable function generator Tacusel IMT-1, connected to a Tacusel PJT 120-1 potentiostat. The working electrode was platinum, with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent/supporting electrolyte. The auxiliary electrode was platinum wire. Tetra-n-butylammonium hexafluorophosphate and dichloromethane were used as supporting electrolyte and solvent in the electrochemical experiments. The system was calibrated ferrocene.

### *Crystal data and data collection for 2*

$C_{18}H_{17}NO_2Fe$, $M=335$, $F(000)=692$. Yellow crystals of **2** suitable for X-ray structural investigations were obtained from slow evaporation of $CH_3OH$ solutions. The plate-like crystals chosen for data collection had dimensions 0.42×0.22×0.22 mm. Unit cell and space group data were obtained on a Rigaku AFC6S four-circle diffractometer, using graphite-monochromated Mo K$\alpha$ radiation at 296 K. Monoclinic space group $P2_1/c$, $a=11.077(9)$, $b=7.430(2)$, $c=19.194(9)$ Å, $\beta=111.02(4)°$, $V=1474(2)$ Å$^3$, $Z=4$, $D_c=1.51$ g cm$^{-3}$, $\mu=10.2$ cm$^{-1}$, min./max. transmission coefficients 0.55/0.92 $\omega$–$2\theta$ scans were used to record the intensities for all non-equivalent reflections with $3.5<2\theta<50°$.

The intensities of three standard reflections showed approximately 11% decay during the data collection for which a decay correction was applied. The data were corrected from Lorentz–polarization effects and empirically (DIFABS) for absorption. Of the 2979 independent intensities, there were 1106 with $F_o^2>2.8\sigma(F_o^2)$, $\sigma(F_o^2)$ being estimated from counting statistics [7]. The scattering factors for all atoms and anomalous dispersion correction terms for Fe were taken from ref. 8.

### *Structure determination of 2 and refinement*

The structure was solved by Patterson and Fourier methods, followed by full-matrix least-squares refinement (TEXSAN). When anisotropic temperature factors were introduced, further difference syntheses permitted location of hydrogen atoms which were included in the calculation. The model converged (max. shift/error = 0.20) to $R=0.038$ and $R_w=0.035$. Final Fourier difference function showed no peaks higher than 0.30 e Å$^{-3}$.

## Results and discussion

### *Crystal structure of 2*

Figure 1 shows a perspective view of the molecule with the atomic numbering scheme. List of atomic coordinates from non-hydrogen atoms are given in Table 1 and selected bond distances and angles are given in Table 2.

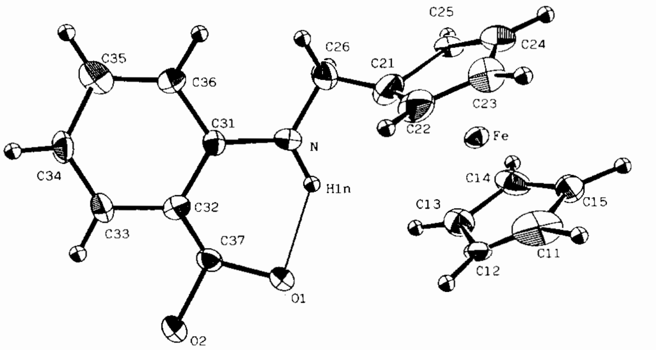

Fig. 1. ORTEP drawing of compound **2** with the atom numbering scheme used.

TABLE 1. Fractional atomic coordinates and thermal parameters[a, b] for compound **2**

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Fe | 0.13557(8) | 0.4865(3) | 0.39639(4) | 2.13(3) |
| O1 | 0.4565(4) | 0.5891(6) | 0.2968(2) | 3.1(2) |
| O2 | 0.6401(4) | 0.5988(6) | 0.2731(2) | 3.4(3) |
| N | 0.4063(5) | 0.2924(7) | 0.3630(3) | 3.2(2) |
| C11 | 0.127(1) | 0.769(2) | 0.4126(4) | 4.9(4) |
| C12 | 0.1838(6) | 0.7430(8) | 0.3623(3) | 2.5(3) |
| C13 | 0.1247(7) | 0.622(1) | 0.2980(3) | 3.3(3) |
| C14 | 0.0001(7) | 0.574(1) | 0.2982(4) | 4.1(3) |
| C15 | −0.0197(7) | 0.677(1) | 0.3575(4) | 3.6(3) |
| C21 | 0.2637(9) | 0.303(1) | 0.4188(5) | 5.1(4) |
| C22 | 0.2969(7) | 0.415(1) | 0.4779(4) | 4.5(3) |
| C23 | 0.1947(7) | 0.424(1) | 0.5044(3) | 3.8(3) |
| C24 | 0.0944(7) | 0.311(1) | 0.4588(4) | 3.5(3) |
| C25 | 0.1010(8) | 0.229(1) | 0.3898(4) | 2.1(3) |
| C26 | 0.3186(6) | 0.179(1) | 0.3817(4) | 3.5(3) |
| C31 | 0.5246(6) | 0.2361(8) | 0.3647(3) | 2.1(2) |
| C32 | 0.6025(6) | 0.3408(8) | 0.3344(3) | 2.2(2) |
| C33 | 0.7220(6) | 0.273(1) | 0.3364(3) | 2.8(3) |
| C34 | 0.7672(6) | 0.112(1) | 0.3691(3) | 3.1(3) |
| C35 | 0.6923(6) | −0.009(3) | 0.3988(3) | 3.4(3) |
| C36 | 0.5745(6) | 0.0668(8) | 0.3966(3) | 2.9(3) |
| C37 | 0.5605(5) | 0.478(2) | 0.3011(3) | 2.3(3) |

[a] e.s.d.s in the last significant digits, as observed from the least-squares refinement, are given in parentheses. [b] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters defined as: $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

TABLE 2. Selected bond distances (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| Fe–C11 | 2.13(1) | Fe–C12 | 2.143(5) |
| Fe–C13 | 2.104(6) | Fe–C14 | 2.050(6) |
| Fe–C15 | 2.144(6) | Fe–C21 | 1.904(7) |
| Fe–C22 | 1.988(6) | Fe–C23 | 1.992(5) |
| Fe–C24 | 1.931(6) | Fe–C25 | 1.947(7) |
| O1–C37 | 1.396(8) | O2–C37 | 1.488(8) |
| N–C26 | 1.426(7) | N–C31 | 1.365(6) |
| C21–C26 | 1.427(9) | C32–C37 | 1.20(1) |
| C26–N–C31 | 123.2(5) | N–C26–C21 | 101.2(6) |
| N–C31–C32 | 122.5(5) | C12–C11–C15 | 94.7(6) |
| N–C31–C36 | 120.2(6) | C32–C31–C36 | 117.3(6) |
| C11–C12–C13 | 120.5(7) | C31–C32–C33 | 119.5(6) |
| C12–C13–C14 | 106.8(6) | C31–C32–C37 | 120.1(6) |
| C13–C14–C15 | 106.9(6) | C33–C32–C37 | 120.0(6) |
| C11–C15–C14 | 108.3(6) | C32–C33–C34 | 121.1(6) |
| C22–C21–C25 | 113.0(7) | C33–C34–C35 | 123.3(9) |
| C22–C21–C26 | 141.6(8) | C34–C35–C36 | 113(2) |
| C25–C21–C26 | 102.2(6) | C31–C36–C35 | 125(1) |
| C21–C22–C23 | 108.7(7) | O1–C37–O2 | 101.8(8) |
| C2–C23–C24 | 108.3(6) | O1–C37–C32 | 133.4(6) |
| C23–C24–C25 | 121.1(7) | O2–C37–C32 | 122.4(6) |
| C21–C25–C24 | 87.8(5) | | |

The structure consists of discrete molecules in which a ferrocenylmethyl framework is attached to the 2-amino-benzoic acid through the nitrogen atom to form a secondary amine derivative. The ferrocene unit shows the expected sandwich conformation with the C11–C15 and C21–C25 rings planar and parallel within experimental error, and the Fe atom lying at 1.712 and 1.485 Å from the mean planes C11–C15 and C21–C25, respectively. As expected the C31–C36 ring is planar and the dihedral angle between this plane and the C21–C25 ring is 80.1°. The Fe–C(Cp-ring) distances range from 1.904(7) to 2.143(5) Å with an average value of 2.033(6) Å. As often observed the cyclopentadienyl rings showed positional disorder which was not important to resolve. It is reflected in a slight dispersion in the intra-Cp C–C bond lengths that range from 1.34(1) to 1.77(1) Å averaging 1.484(9) Å. An intramolecular hydrogen bond N–H1n···O1 is observed.

### *Spectroscopic characterization and electrochemical behaviour*

Ferrocene-containing ligands can be synthesized by means of a wide variety of reactions depending on the starting ferrocene derivative. For instance, Schiff base ferrocene-containing groups could be obtained by reaction of ferrocenecarboxaldehyde or ferrocenylamine with an appropriate amine [6, 9] or aldehyde [10], respectively. However the stability of the resulting imines towards hydrolysis is a problem for using them as ligands. However this problem can be avoided by hydrogenation of the imines to yield the parent amines which have to be more stable in solution.

The well-known 2-amino-benzoic acid ligand has been used as a starting material together with ferrocenecarboxaldehyde to yield the Schiff base complex 2-ferrocenylmethylidenimino-benzoic acid (**1**). Analytical and spectroscopic data are in agreement with the proposed formulation of **1**. The IR spectrum of **1** shows no peaks in the N–H absorption zone and a strong $\nu$(C=N) imine stretching vibration occurs at 1603 cm$^{-1}$. Compound **1** is a potential N,O-donor bidentate ferrocene-containing ligand. However preliminary studies on solutions of **1** shows that its use as a ligand is hindered by presence of a hydrolytic reaction especially in the presence of water or metal ions. In order to increase the stability of this compound in solution, the imino group was reduced by using $NaBH_4$. The hydrogenation was carried out in tetrahydrofuran and the dark red solution becomes yellow from where the compound 2-ferrocenylmethylamino-benzoic acid (**2**) was isolated. IR spectroscopic studies on **2** revealed that the imino group in **1** was reduced as shown by the lack of $\nu$(C=N) imine stretching peak and the occurrence of a $\nu$(N–H) stretching vibration at 3346 $cm^{-1}$. Furthermore the presence of characteristic carboxylic group absorptions indicates that the reaction was performed selectively and no reduction of the acid group occurs. IR also displays several characteristic ferrocene absorptions in both cases [11].

$^1H$ NMR spectra of **1** and **2** show three resonances for the ferrocenyl protons (one and two signals for the unsubstituted and substituted rings, respectively) in 5:2:2 ratio and four signals (two triplets and two doublets) observed in the 6.5–8.3 range were assigned to the phenyl protons. Additionally a low-field signal in **1** for the methylidene proton and a high-field signal in **2** for the methylene protons were also detected. In the $^{13}C\{^1H\}$ NMR spectrum of **1** and **2** four signals were observed in the region assigned to the cyclopentadienyl rings, the low-field signal being attributed to the *ipso* carbon. Several signals appeared in the phenyl carbon region and two additional resonances at 146.73 and 41.29 ppm were observed for **1** and **2**, respectively, assigned to the methylidene and methylene carbons. In both cases the lowest field resonance was assigned to the carboxylic group.

The electrochemical behaviour by cyclic voltammetry (0.1 M $NBu^n{}_4PF_6$, $CH_2Cl_2$) at room temperature of **1** and **2** was investigated. **1** shows a monoelectronic oxidation peak at a value ($E_{pa} = 0.74$ V) close to that found for ferrocenecarboxaldehyde (0.77 V). This contrasts with the oxidation potential value obtained in the related compound *N,N'*-ethylenebis(ferrocenylmethylidenimine) [6] where a decrease of 170 mV in the oxidation potential was found compared with the ferrocenecarboxaldehyde, the only difference between both compounds being the shift from aryl to alkyl attached to the Schiff base fragment. The difference between the anodic and cathodic peak potentials ($\Delta E_p = 167$ mV) as well as the ratio between cathodic and anodic intensities ($i_c/i_a = 0.6$) in **1** are far from that expected for a reversible process (ferrocene gives in the same conditions $\Delta E_p = 78$ mV and $i_c/i_a = 1$) indicating an important degree of irreversibility. In contrast **2** shows a monoelectronic reversible oxidation peak at 0.51 V with $\Delta E_p = 80$ mV ad ratio of intensities $i_c/i_a = 1$, the oxidation potential being in good agreement with other reported values for compounds containing a ferrocenylmethylamino group [6].

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