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Note

Synthesis, properties and crystal structures of ferrocene derivatives containing pyrazinium and quinoxalinium units

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Dedicated to Prof. Dr. Dirk Steinborn on the occasion of his 60th birthday.

Abstract

The pyrazinium salt [$FcCH_2pyz$][BF_4] (**1**) and the quinoxalinium salt [$FcCH_2quin$][BF_4] (**2**) were prepared by the reaction of [$FcCH_2$][BF_4] with pyrazine and quinoxaline, respectively and characterised by spectroscopic methods, cyclic voltammetry and by single-crystal X-ray diffraction, which revealed the absence of any π–π-stacking motifs in the crystal structures.

Keywords: Iron; Electrochemistry; X-ray crystal structure

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1. Introduction

Ferrocene derivatives which contain quaternised cationic nitrogen heterocycles such as, for example, pyridinium (py) or 4,4′-bipyridinium (bipy) exhibit interesting properties which have been investigated in various supramolecular contexts like molecular recognition of DNA [1], redox sensing of anions in solution [2] and preparation of TCNQ radical ion salts with special magnetic behaviour [3]. We here report on ferrocene derivatives which contain the particularly electron-poor pyrazinium (pyz) and quinoxalinium (quin) units.

2. Results and discussion

[$FcCH_2pyz$][BF_4] (**1**) and [$FcCH_2quin$][BF_4] (**2**) were prepared straightforwardly by the reaction of [$FcCH_2$][BF_4] (generated in situ from $FcCH_2OH$ and tetrafluoroboric acid [4]) with pyrazine and quinoxaline, respectively (Scheme 1). This synthetic strategy had already been used previously for the preparation of [$FcCH_2py$][BF_4] (py = pyridine) [5]. Both new compounds were obtained as orange crystalline solids in ca. 60 % yield. They are slightly soluble in dichloromethane and moderately soluble in more polar organic solvents like acetone and acetonitrile. In each case, the CH_2 group gives rise to a resonance signal close to 6 ppm in the ^1H NMR spectrum; the corresponding ^{13}C NMR signal lies close to 60 ppm. These values compare well with those of closely related species such as, for example, [$FcCH_2py$]$^+$ [6] and [$FcCH_2bipy$]$^+$ [7]. Owing to the quadrupole moment of ^{14}N ($I = 1$), the ^{13}C NMR signal of the tertiary carbon atom adjacent to the formally cationic alkylated N atom of **2** shows characteristic broadening; in the case of **1** ^{14}N, ^{13}C coupling is resolved (t, $^1J = 9$ Hz) for the magnetically equivalent tertiary carbon atoms bonded to the alkylated N atom.

The structures of **1** and **2** were investigated by single-crystal X-ray diffraction (Figs. 1 and 2). We note that π–π-stacking motifs are absent in the crystal structures of both compounds. The cyclopentadienyl rings are in an essentially eclipsed orientation in each case (cyclopentadienyl twist angles <3°), and the cationic substituent is pointing away from the ferrocene. The angle between the

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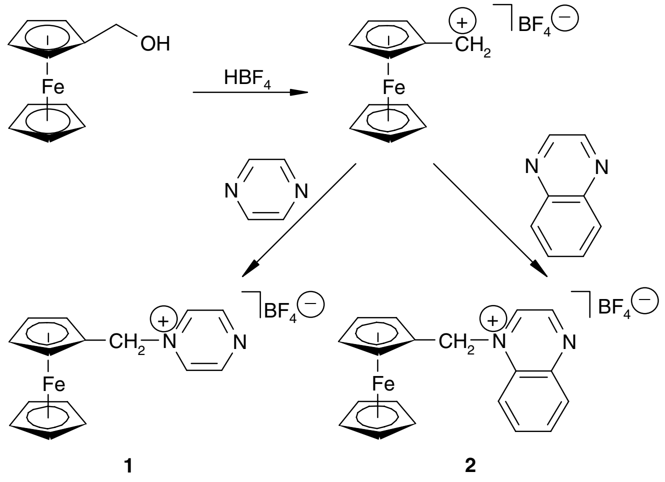

Scheme 1.

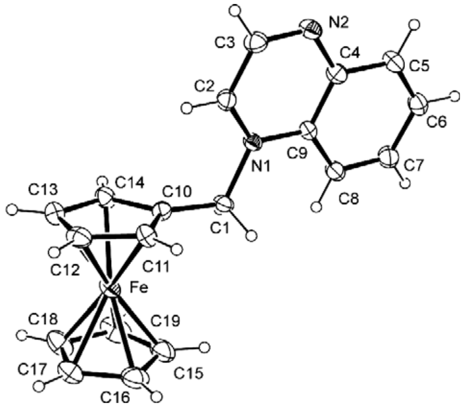

Fig. 2. Molecular structure of **2**, showing the atom-labelling scheme. The tetrafluoroborate anion is not shown. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are drawn as circles of arbitrary radius.

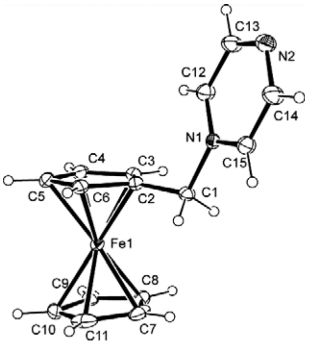

Fig. 1. Molecular structure of **1**, showing the atom-labelling scheme. The tetrafluoroborate anion and solvent molecule are not shown. Displacement ellipsoids are drawn at the 30% probability level except for the H atoms, which are drawn as circles of arbitrary radius.

C_{ipso}–CH_2 vector and the plane of the substituted cyclopentadienyl ring is 6.1(2)° for **1** and 2.8(4)° for **2**. The angles formed by the ring plane of the heterocyclic substituent and the plane of the corresponding substituted cyclopentadienyl ring are 76.39(8)° and 85.8(1)° for **1** and **2**, respectively. The bond lengths of the pyrazinium unit of **1** are similar to those found for other alkylated pyrazine derivatives such as, for example, $[pyz(CH_2)_3pyz]Br_2$ [8] and [Etpyz]$(TCNQ)_3$ [9]. Likewise, the bond lengths of the quinoxalinium unit of **2** are similar to those found for the related [*n*-Prquin]TCNQ [10]. The C–N and C–C bond lengths of the CH_2 group are 1.512(3) and 1.494(3) Å, respectively, for **1** and 1.484(6) and 1.524(5) Å, respectively, for **2**. These values are similar to the corresponding bond lengths of 1.490(5) and 1.488(5) Å found for the pyridinium salt $[FcCH_2py]I$ [11].

Several weak C–H···F interactions between the cation and the tetrafluoroborate anion are observed for both compounds [12]. In the case of compound **1**, three H···F distances are present which are considerably lower than the sum of the van der Waals radii (2.54 Å) and fall in the range between 2.32 Å and 2.42 Å. Four such distances are observed for compound **2**, which lie between 2.17 Å and 2.39 Å. These interactions lead to a range of C···F distances slightly above 3.0 Å and C–H···F angles between ca. 133° and 167°.

UV–Vis spectroscopic data for **1** and **2** have been obtained in dichloromethane solution. Both compounds exhibit strong absorption bands in the UV region due to the heterocyclic ring system ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions). **1** has absorption maxima at 226 nm ($\lg\varepsilon = 3.5$), 264 nm ($\lg\varepsilon = 3.6$) and 432 nm ($\lg\varepsilon = 1.8$). The absorption maxima of **2** are located at 238 nm ($\lg\varepsilon = 4.2$), 318 nm ($\lg\varepsilon = 3.5$) and 448 nm ($\lg\varepsilon = 1.6$). The UV absorption data are similar to those observed for related compounds such as, for example, [Etpyz]Br ($\lambda_{max} = 272$ nm, $\lg\varepsilon = 3.9$) and [Etquin′]I (quin′ = 2,3-dimethylquinoxalinium) ($\lambda_{max} = 259$ nm, $\lg\varepsilon = 4.6$; $\lambda_{max} = 377$ nm, $\lg\varepsilon = 4.0$) [13]. The weak absorption band in the visible region is due to the ferrocene moiety. For pristine ferrocene, this band has previously been assigned to the $^1A_{1g} \rightarrow {}^1E_{2g}$ ligand-field transition in D_{5d} symmetry [14]. There is no indication for any absorption band due to charge transfer from the ferrocenyl moiety to the cationic heterocyclic substituent.

Compounds **1** and **2** each contain two potentially redox-active moieties and multiple redox states may be expected for both compounds. Their redox-chemical behaviour was probed by cyclic voltammetry in dichloromethane solution containing 0.13 M n-Bu_4NBF_4 as supporting electrolyte. A ferrocenyl-based chemically and electrochemically reversible one-electron oxidation is observed for both compounds. Owing to the presence of the cationic substituent, this oxidation is more difficult than that of pristine ferrocene ($E^{0'} = 0.24$ V vs. ferrocenium/ferrocene for both compounds). An irreversible reduction of the cationic heterocycle present in these species occurs at $E_{1/2} = -1.07$ V for **1** and at $E_{1/2} = -0.74$ V for **2**.

It is possible to dialkylate pyrazine and quinoxaline by using Meerwein salts, whereas less potent alkylating agents

Table 1
Crystal data and structure refinement for **1** and **2**

Compound	$[FcCH_2pyz][BF_4]$ (**1**)	$[FcCH_2quin][BF_4]$ (**2**)
Empirical formula	$C_{15}H_{15}BF_4FeN_2 \cdot 0.5CH_2Cl_2$	$C_{19}H_{17}BF_4FeN_2$
Formula weight	408.41	416.01
Temperature (K)	133(2)	133(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Ama*2	$P2_1/c$
Lattice parameters		
length (Å)	$a = 23.968(2)$	$a = 21.769(3)$
	$b = 23.2634(16)$	$b = 7.2808(9)$
	$c = 5.9807(4)$	$c = 11.335(2)$
angle (°)		$\beta = 92.495(15)$
Cell volume (Å^3)	3334.7(4)	1794.9(5)
Z	8	4
$D_{calc.}$ (g cm^{-3})	1.627	1.539
μ (mm^{-1})	1.105	0.885
$F(000)$	1665	848
θ Range (°)	1.7–25.0	1.87–25.0
Index ranges	$-28 \to h \to 28$	$-25 \to h \to 24$
	$-24 \to k \to 27$	$-8 \to k \to 8$
	$-6 \to l \to 7$	$-13 \to l \to 13$
Reflections collected	8448	10720
Independent reflections [R_{int}]	2865 [0.0572]	3156 [0.1040]
Reflections observed	2664	1725
T_{min}/T_{max}	0.61/0.91	0.80/0.95
Data/restraints/parameters	2865/1/246	3156/0/245
Goodness-of-fit on F^2	1.011	0.846
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0275$, $wR_2 = 0.0676$	$R_1 = 0.0520$, $wR_2 = 0.0867$
R indices (all data)	$R_1 = 0.0299$, $wR_2 = 0.0684$	$R_1 = 0.1107$, $wR_2 = 0.0991$
Extinction coefficient	–	0.0024(5)
Largest difference in peak and hole (e Å^{-3})	0.364 and −0.411	0.384 and −0.389

only lead to monoalkylation [15]. These dications are easily reduced to pertinent radical monocations [16]. We anticipated therefore that in the case of **1** and **2** such a procedure would instantaneously result in a valence tautomerisation of the dication by electron transfer from the ferrocenyl group to the dicationic heterocyclic substituent. Unfortunately, however, our attempts to alkylate the second N atom present in **1** and **2**, respectively, by using $[OR_3][BF_4]$ (R = Me, Et) afforded only intractable material.

3. Experimental section

All reactions were performed in an inert atmosphere (dinitrogen) by using standard Schlenk techniques; work-up was performed in the air. Solvents and reagents were procured from standard commercial sources. Hydroxymethylferrocene was prepared by using an established route [17]. NMR spectra were recorded with a Varian Unity INOVA 500 (500.13 MHz for ^{1}H). Elemental analyses were performed by the microanalytical laboratory of the University of Halle.

3.1. Synthesis of **1**

Tetrafluoroboric acid (4.0 ml, 50% aqueous solution) was added dropwise at −30 °C to a stirred solution of hydroxymethylferrocene (2.16 g, 10.0 mmol) in dichlormethane (40 ml). After 45 min pyrazine (1.00 g, 12.5 mmol) was added in small portions. The mixture was subsequently allowed to warm to room temperature. After 12 h the organic layer was separated off. The aqueous phase was extracted with dichloromethane until the extracts were colourless. The combined organic layers were dried with sodium sulfate. The volume of the solution was reduced to ca. 50 ml in vacuo. Crystallisation at −40 °C afforded the product as an orange crystalline solid. Yield 2.31 g (63%). Anal. Found: C, 49.99; H, 5.11; N, 7.62. Calc. for $C_{15}H_{15}N_2BF_4Fe$ (365.95): C, 49.23; H, 4.13; N, 7.66%. ^{1}H NMR (acetone-d_6): $\delta = 4.33$ (s, 5H, Cp); 4.38, 4.70 (2m, 2 × 2H, $C_5\mathit{H}_4CH_2$pyz); 5.95 (s, 2H, CH_2); 9.12, 9.53 (2m, 2 × 2H, pyz). $^{13}C\{^1H\}$ NMR (acetone-d_6): $\delta = 64.2$ (CH_2); 71.1 (Cp); 72.2, 72.3 (tert. $\mathit{C}_5H_4CH_2$pyz); 79.6 (quart. C_5H_4-CH_2pyz); 138.1 (t, $^1J(^{14}N, ^{13}C) = 9$ Hz, pyz); 152.9 (pyz).

3.2. Synthesis of **2**

2.25 g (54%) of **2** were obtained as an orange, crystalline solid from hydroxymethylferrocene (2.16 g, 10.0 mmol) and quinoxaline (1.60 g, 12.3 mmol) by a procedure analogous to that described for **1**. Anal. Found: C, 54.63; H, 4.26; N, 6.67. Calc. for $C_{19}H_{17}N_2BF_4Fe$ (416.01): C, 54.86; H, 4.12; N, 6.73%. ^{1}H NMR (acetone-d_6): $\delta = 4.41$ (s, 5H, Cp); 4.43, 4.73 (2m, 2 × 2H, $C_5\mathit{H}_4CH_2$quin); 6.39 (s, 2H, CH_2); 8.35, 8.43, 8.55, 9.06 (4m, 4 × 1H, quin); 9.32, 9.68 (2d, $^3J = 2.9$ Hz, 2 × 1H, quin). $^{13}C\{^1H\}$ NMR (acetone-d_6): $\delta = 59.8$ (CH_2); 71.0 (Cp); 71.9, 72.4 (tert. $\mathit{C}_5H_4CH_2$quin); 78.3 (quart. $\mathit{C}_5H_4CH_2$quin); 121.0, 132.3, 133.0, 135.4, 137.6, 140.0 (br.), 147.8, 149.5 (quin).

4. Crystal structure determinations

For each data collection a single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample. Data collection using Mo Kα radiation ($\lambda = 0.71073$ Å) was made on a Stoe IPDS2 diffractometer equipped with a two-circle goniometer and an area detector. Absorption correction was done by integration using X-red [18]. The data sets were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least squares refinements against F^2 (SHELXL97) [19]. All non-H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2-fold isotropic displacement parameters. Pertinent crystallographic data are collected in Table 1. Graphical representations were made using ORTEP-3 win [20].

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 604268 (**2**) and 604269 (**1**). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 33603; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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