

Synthesis, crystal structures, and electrospray ionisation mass spectrometry investigations of ether- and thioether-substituted ferrocenes

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A number of ether- and thioether-substituted ferrocenes (1,1'-bis(1,3-dioxane-2-yl)ferrocene **1**, 1,1'-bis(5-methyl-1,3-dioxane-2-yl)ferrocene **2**, 1,1'-bis(4-methyl-1,3-dioxane-2-yl)ferrocene **3**, 1,1'-bis[(*R*)-(–)-4-methyl-1,3-dioxane-2-yl]ferrocene **4**, 1,1'-bis(4,6-dimethyl-1,3-dioxane-2-yl)ferrocene **5**, and 1,1'-bis(1,3-dithiane-2-yl)ferrocene **6**) were synthesised by direct condensation of 1,1'-diformylferrocene with the corresponding diols or dithiols. The crystal structures of **1**, **5a**, **5b**, and **6** were determined by X-ray diffraction studies. Electrospray ionisation mass spectrometry was used to investigate the binding behaviour of **1** and **6** toward alkali as well as transition metal cations. The dioxane-containing species **1** showed high affinity toward Li^+ and Na^+ , whereas the dithiane derivative **6** bound, as expected, preferentially to Hg^{2+} .

1 Introduction

The advanced features of ferrocene regarding the chemical stability as well as the well defined chemistry but also the special electrochemical behaviour moved the main representative out of the metallocene-group into the scope of synthetic chemists, material chemists, and catalysis researchers.^{1,2} For the latter the introduction of chirality is a main concern. This can be realised *via* two principle pathways: (i) substitution of ferrocene with asymmetric units or (ii) introduction of planar chirality to the ferrocene unit. In a few cases the formation of hybrid molecules, *i.e.*, combination of both chiral elements, led to preferable catalytic as well as coordinative properties of ferrocene-derivatives (*e.g.*, *P,N*-chelate formation *via* derivatisation with a diphenylphosphino-group).³

The method of choice for the introduction of planar chirality to ferrocene was reported by Ugi *et al.* in the early 1970s. It implies the diastereoselective *ortho*-lithiation of (*R*)-*N,N*-dimethyl-1-ferrocenyl ethyl amine with high diastereomeric excess (92%).^{4,5} In the 1990s several new, highly efficient methods for *ortho*-directions of secondary substitutions on ferrocene were reported with most of them exploiting the *ortho*-directing properties of chiral, heteroatom-containing functionalities, *e.g.*, amines, dioxanes, sulfoxides, or oxazolines.^{6–12} The investigations of Kagan's group on the *ortho*-direction of Li^+ by dioxane-substituted ferrocenes which led to regioselective electrophilic substitution in the *ortho*-position should be emphasised due to the relation to the present work.

The sulfur-analogues of the dioxanes – the dithianes – display strong affinity toward transition metals (following the principle of hard and soft acids and bases – HSAB). Williams and co-workers investigated the metal-binding behaviour of thiacrown ethers with mercury(II), lead(II), cadmium(II), and zinc(II) ions by mass spectrometry.¹³ They found high selectivity toward Hg^{2+} dependent on the size as well as on the combination of heteroatoms in the ring.

Beside the determination of binding properties, electrospray ionisation mass spectrometry (ESI-MS) was proven to be a useful technique for the characterisation of metal complexes with sulfur-containing macrocycles, *e.g.*, Cr,¹⁴ Pd(II), Pt(II),¹⁵ Ru(II).¹⁶

Iwanek *et al.* studied the complexation of alkali, several transition metal, and tetramethyl ammonium as well as guanidinium and ammonium cations to crown ether analogues bearing methoxy substituents by ESI-MS.¹⁷ The observed

selectivity toward the guanidinium cation is of special interest with respect to biological and medicinal applications.^{18,19}

ESI-MS delivers fast and reliable information about molecular weight, charge, as well as isotope distribution of molecules and is due to the softness of the ionisation of special interest for coordination chemistry researchers.

Herein we report the synthesis and characterisation of 1,1'-bis(dioxane-2-yl)ferrocene and derivatives as well as 1,1'-bis(dithiane-2-yl)ferrocene. Additionally, the molecular structures of 1,1'-bis(1,3-dioxane-2-yl)ferrocene **1**, 1,1'-bis[(4*R*,6*S*)-4,6-dimethyl-1,3-dioxane-2-yl]ferrocene **5a**, 1-[(4*R*,6*S*)-4,6-dimethyl-1,3-dioxane-2-yl]-1'-(4,6-dimethyl-1,3-dioxane-2-yl)ferrocene **5b**, and 1,1'-bis(1,3-dithiane-2-yl)ferrocene **6** were determined by single crystal X-ray diffraction analyses. The affinity of the newly developed ligands **1** and **6** toward alkali as well as transition metal ions was assayed by ESI-MS in acetone–water mixtures.

2 Experimental

All syntheses were carried out in dry solvents and under argon atmosphere. The NMR-spectra were recorded on a Bruker DPX 400 instrument (Ultraschield™ Magnet) at 400.13 MHz (¹H) and 100.63 MHz (¹³C) at 298 K in CDCl₃ with 1% of tetramethylsilane as internal standard. Chemical shifts are reported relative to TMS and coupling constants are in Hz. Mass spectra were measured on a Bruker esquire₃₀₀₀ (ESI). The samples for affinity investigations by mass spectrometry were prepared to yield molar ratios of 0.5 : 1, 1 : 1 and 10 : 1 (metal ion to ligand), the solvent system was a mixture of H₂O and acetone (1 : 1). The detailed measurement parameters which were optimised for the ligand peaks are listed in Table 1. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. The elemental analyses were performed by the Laboratory for Elemental Analysis of the Department of Physical Chemistry, University of Vienna, with a Perkin Elmer 2400 CHN Elemental Analyzer. Silica gel was used for both column chromatography (Fluka-60, 70–230 mesh) and thin layer chromatography (Polygram® SIL G/UV₂₅₄). X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer at 120 K for **1** and 110 K for **5a**, **5b**, and **6** (for crystal structures see Figs. 2–5). Single crystals were positioned at 40, 35, 35 and 35 mm from the detector and 771, 200, 150, and 327 frames were measured, each for 100, 55, 55, and

Table 1 Operational MS parameters optimised for the detection of the ligands **1** and **6**

Parameters	1	6
HV capillary/V	4500	4500
Dry gas flow/l min ⁻¹	5	5
Dry gas temperature/°C	120	120
Nebulizer gas/psi	10	10
Skimmer I/V	36.1	39.4
Capillary exit offset/V	73.7	75.3
Octopole/V	2.51	2.56
Octopole Δ /V	2.40	2.40
Trap drive/V	30.9	33.2
Injection rate/ μ l min ⁻¹	3	3
Polarity	Positive	Positive
Scan range / m/z	50–1000	50–1000

100 s over 1, 1.5, 1.5, and 2 degree scan for **1**, **5a**, **5b**, and **6**, correspondingly. The data were processed using Denzo-SMN software. Crystal data, data collection parameters, and structure refinement details for **1**, **5a**, **5b**, and **6** are given in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were located on difference Fourier maps and refined isotropically [**5a**, **5b**, and **6** (except the disordered fragment)], or placed at calculated positions and refined as riding atoms in the subsequent least squares model refinement (**1**). Their isotropic thermal parameter was estimated to be 1.2 times the value of the equivalent isotropic thermal parameter of the atom to which hydrogen was bound.

CCDC reference numbers 208189 (**1**), 208190 (**5a**), 208191 (**5b**), 208192 (**6**).

See <http://www.rsc.org/suppdata/dt/b3/b304115h/> for crystallographic data in CIF or other electronic format.

General procedure for the synthesis of the ligands

The corresponding diols or the dithiol (4 mmol), molecular sieves (4 Å) and *p*-toluenesulfonic acid monohydrate (0.4 mmol) were added to a solution of 1,1'-diformylferrocene (2 mmol) in toluene (15 ml). This reaction mixture was stirred for 24 h at 60 °C, cooled down and solid, anhydrous potassium carbonate (10 mmol) was added. Afterwards the reaction mixture was filtered through Celite® and purified by column chromatography (hexane : ethyl acetate = 3 : 1).

1,1'-Bis(1,3-dioxane-2-yl)ferrocene 1. Yield: 63%; m.p. 110–111 °C; ¹H NMR (CDCl₃) δ : 5.42 (s, 2H, CHO₂), 4.33 (brs, 4H, Fc–H), 4.22 (dd, 4H, CH₂O, *J* = 4.5, 11.0 Hz), 4.17 (brs, 4H, Fc–H), 3.94 (tr, 4H, CH₂O, *J* = 11.0 Hz), 2.17 (m, 2H, CH₂), 1.40 (d, 2H, CH₂, *J* = 13.0 Hz); ¹³C {¹H} NMR (CDCl₃)

δ : 100.87 (CHO₂), 86.94 (Cp), 69.34 (Cp), 67.77 (Cp), 67.65 (OCH₂), 26.24 (CH₂). Anal. calcd. for C₁₈H₂₂FeO₄: C 60.19, H 6.19. Found: C 60.14, H 5.98. MS (ESI⁺): [C₁₈H₂₂FeO₄ + H]⁺ m/z 359.

1,1'-Bis(5-methyl-1,3-dioxane-2-yl)ferrocene 2. Yield: 50%; m.p. 164–165 °C; ¹H NMR (CDCl₃) δ : 5.33 (s, 2H, CHO₂), 4.33 (brs, 4H, Fc–H), 4.17–3.91 (m, 8H, Cp, CH₂O), 3.45 (tr, 4H, CH₂O, *J* = 11.0 Hz), 2.18 (m, 2H, CH), 0.76 (d, 6H, CH₃, *J* = 6.0 Hz); ¹³C {¹H} NMR (CDCl₃) δ : 100.50 (CHO₂), 86.68 (Cp), 73.98 (CH₂O), 69.36 (Cp), 67.84 (Cp), 29.76 (CH), 12.81 (CH₃). Anal. calcd. for C₂₀H₂₆FeO₄: C 62.16, H 6.79. Found: C 62.13, H 6.84. MS (ESI⁺): [C₂₀H₂₆FeO₄ + H]⁺ m/z 387.

1,1'-Bis(4-methyl-1,3-dioxane-2-yl)ferrocene 3. Yield: 81%; m.p. 98–99 °C; ¹H NMR (CDCl₃) δ : 5.42 (s, 2H, CHO₂), 4.34 (brs, 4H, Fc–H), 4.20 (dd, 2H, CHO, *J* = 4.0, 11.0 Hz), 4.16 (brs, 4H, Fc–H), 3.90 (m, 4H, CH₂O), 1.74 (m, 2H, CH₂), 1.49 (m, 2H, CH₂), 1.31 (d, 6H, CH₃, *J* = 6.5 Hz); ¹³C {¹H} NMR (CDCl₃) δ : 100.51 (CHO₂), 87.04 (Cp), 73.50 (Cp), 69.35 (Cp), 69.28 (Cp), 68.17 (CHCH₃O), 67.97 (CHCH₃O), 67.38 (OCH₂), 33.44 (CH₂), 23.34 (CH₃). Anal. calcd. for C₂₀H₂₆FeO₄: C 62.16, H 6.79. Found: C 61.97, H 6.70. MS (ESI⁺): [C₂₀H₂₆FeO₄ + H]⁺ m/z 387.

1,1'-Bis[(*R*)-(–)-4-methyl-1,3-dioxane-2-yl]ferrocene 4. Yield: 57%; m.p. 97–98 °C; ¹H NMR (CDCl₃) δ : 5.42 (s, 2H, CHO₂), 4.35 (brs, 4H, Fc–H), 4.20 (dd, 2H, CHO, *J* = 4.0, 11.0 Hz), 4.17 (brs, 4H, Fc–H), 3.90 (m, 4H, CH₂O), 1.74 (m, 2H, CH₂), 1.49 (m, 2H, CH₂), 1.31 (d, 6H, CH₃, *J* = 6.5 Hz); ¹³C {¹H} NMR (CDCl₃) δ : 100.53 (CHO₂), 87.08 (Cp), 73.50 (Cp), 69.47 (Cp), 69.39 (Cp), 68.27 (CHCH₃O), 68.03 (CHCH₃O), 67.39 (OCH₂), 33.43 (CH₂), 22.35 (CH₃). Anal. calcd. for C₂₀H₂₆FeO₄: C 62.16, H 6.79. Found: C 62.11, H 6.73. MS (ESI⁺): [C₂₀H₂₆FeO₄ + H]⁺ m/z 387.

1,1'-Bis(4,6-dimethyl-1,3-dioxane-2-yl)ferrocene 5. Yield: 61% (mixture of isomers); m.p. 113–114 °C; ¹H NMR (CDCl₃) δ : 5.44 (s, 2H, CHO₂), 4.35 (brs, 4H, Fc–H), 4.13 (brs, 4H, Cp), 3.89 (m, 4H, CHO), 1.57 (m, 2H, CH₂), 1.49 (d, 2H, CH₂, *J* = 6.6), 1.36 (d, 12H, CH₃, *J* = 6.6 Hz); ¹³C {¹H} NMR (CDCl₃) δ : 100.11 (CHO₂), 87.14 (Cp), 73.16 (CHCH₃O), 69.33 (Cp), 68.41 (Cp), 40.81 (CH₂), 22.21 (CH₃). Anal. calcd. for C₂₂H₃₀FeO₄: C 63.75, H 7.30. Found: C 63.95, H 7.36. MS (ESI⁺): [C₂₂H₃₀FeO₄ + H]⁺ m/z 415.

1,1'-Bis(1,3-dithiane-2-yl)ferrocene 6. Yield: 75%; m.p. 137–138 °C; ¹H NMR (CDCl₃) δ : 5.07 (s, 2H, CHS₂), 4.43 (brs, 4H, Fc–H), 4.29 (brs, 4H, Fc–H), 3.03 (tr, 4H, CH₂S, *J* = 12.3 Hz), 2.85 (dd, 4H, CH₂S, *J* = 3.3, 11.0 Hz), 2.15 (m, 2H, CH₂), 1.89 (m, 2H, CH₂); ¹³C {¹H} NMR (CDCl₃) δ : 87.87 (Cp), 69.73

Table 2 Crystallographic data for **1**, **5a**, **5b**, and **6**

Compound	1	5a	5b	6
Chemical formula	C ₁₈ H ₂₂ FeO ₄	C ₂₂ H ₃₀ FeO ₄	C ₂₂ H ₃₀ FeO ₄	C ₁₈ H ₂₂ FeS ₄
Formula weight	358.21	414.31	414.31	422.45
<i>T</i> /K	120	110	110	120
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>Cc</i>
<i>a</i> /Å	5.886(1)	10.2611(2)	10.2840(4)	12.203(2)
<i>b</i> /Å	27.628(6)	10.3294(2)	10.9921(3)	18.686(4)
<i>c</i> /Å	9.673(2)	19.0505(4)	17.9147(7)	9.861(2)
β /°	93.50(3)			125.43(3)
<i>V</i> /Å ³	1570.1(5)	2019.18(7)	2025.13(12)	1832.2(6)
<i>Z</i>	4	4	4	4
μ_{calcd} /cm ⁻¹	9.78	7.71	7.69	12.75
Flack parameter		0.013(9)	–0.006(16)	0.435(12)
<i>R</i> ₁ ^a	0.0367	0.0248	0.0448	0.0324
<i>wR</i> ₂ ^b	0.0867	0.0512	0.0770	0.0623

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w|F_o|^2 - |F_c|^2] / \sum w|F_o|^2]^{1/2}$.

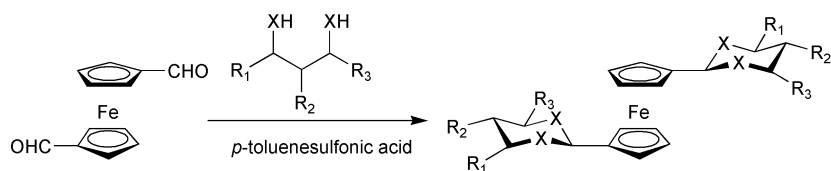


Fig. 1 General scheme for the synthesis of the title compounds and list of the synthesised compounds.

(Cp), 68.94 (Cp), 47.41 (CHS₂), 32.28 (SCH₂), 25.88 (CH₂). Anal. calcd. for C₁₈H₂₂FeS₄: C 51.21, H 5.17, S 30.53. Found: C 51.19, H 5.25, S 30.31. MS (ESI⁺): [C₁₈H₂₂FeS₄ + H]⁺ *m/z* 423.

3 Results and discussion

Synthesis

The dioxanes as well as the dithiane derivatives were synthesised by a straightforward condensation reaction between 1,1'-diformylferrocene and the diol or dithiol in dry toluene under argon-atmosphere. The reactions were carried out in the presence of a catalytic amount of *p*-toluenesulfonic acid at 60 °C for 24 h (see Fig. 1).

The preparation of monodioxane-2-yl-ferrocenes is well documented. It involves the synthesis of ferrocenyl dimethyl acetal in a first step followed by addition of an appropriate diol, *e.g.*, 1,3-butanediol, in chloroform with a catalytic amount of *p*-toluenesulfonic acid to form a six-membered ring in a second step.^{7,20} In this work we developed an alternative one step procedure which is less time-consuming (because of excluding the methyl acetal isolation stage) and resulting in high yields of the final products.

The formation of the dioxanes from the corresponding chiral diols proceeds without inversion at the chiral centre. The reaction of 1,1'-diformylferrocene with enantiomerically pure (*R*)-(-)-1,3-butanediol yielded 1,1'-bis[(*R*)-(-)-4-methyl-1,3-dioxane-2-yl]ferrocene **4** in 57% yield. The use of racemic diols resulted in racemic mixtures of dioxanes. In the case of 1,1'-bis(4,6-dimethyl-1,3-dioxane-2-yl)ferrocene **5**, *i.e.*, the product of the condensation of 1,1'-diformylferrocene with racemic 2,4-pentanediol, we isolated single crystals of two diastereomers by column chromatography on silica (for crystal structures see Figs. 3 and 4).

The formation of the dioxane or dithiane rings can successfully be monitored by ¹H- and ¹³C-NMR spectroscopy. The ¹H and the ¹³C resonances of the hydrogen and carbon atoms of the -CHO group are shifted upfield when the aldehyde group is converted into a hemiacetal and subsequently into an acetal functionality. A shift from about 10.0 ppm (aldehyde) *via* 7.0 ppm (hemiacetal) to *ca.* 5.4 ppm (acetal) and 5.0 ppm (thioacetal) was observed in ¹H-NMR spectra. Analogously the carbon resonance is shifted upfield from about 190 ppm (aldehyde) to *ca.* 100 ppm (acetal). The shift is even stronger in the case of **6** where the signal was observed at 47.41 ppm – this is in good agreement to literature data.^{21–23}

Crystal structure determination

The molecular structures of **1** and **6** are shown in Fig. 2 (for selected bond lengths for compounds **1**, **5a**, **5b**, and **6** see Table 3). The Cp rings adopt substantially different arrangements in **1** and **6**: approaching the conformation between anticlinal staggered and synclinal eclipsed in **6** (the torsional angle C1–X1a–X1b–C10 is –90.1°) and anticlinal in **1** (the torsional angle is 141.3°). Both dioxane rings in **1** and dithiane rings in **6** assume a chair conformation with the Cp substituents in an equatorial orientation. The atoms O1, O2, C7, C9 in **1** and S1, S2, C7, C9 in **6** are coplanar, respectively, within ±0.003 and ±0.006 Å. The atoms C6 and C8 are on opposite sides of these mean planes at –0.649 and 0.678 Å in **1** and 0.833 and –0.726 Å in **6**. Likewise, the atoms O3, O4, C16, C18 and S3, S4, C16, C18 are coplanar within ±0.006 Å both in **1** and **6**, with deviation of C15 and C17

Table 3 Bond lengths (Å) in the dioxane/dithiane rings of **1**, **5a**, **5b**, and **6**

Atom 1–atom 2	1	5a	5b	6
C6–O1/S1	1.421(2)	1.4075(19)	1.408(3)	1.828(3)
O1/S1–C7	1.442(3)	1.4429(18)	1.443(3)	1.813(3)
C7–C8	1.507(4)	1.518(2)	1.520(4)	1.510(4)
C8–C9	1.509(3)	1.516(2)	1.509(4)	1.517(4)
C9–O2/S2	1.436(3)	1.4436(17)	1.447(3)	1.807(3)
O2/S2–C6	1.406(2)	1.4255(17)	1.414(3)	1.813(3)

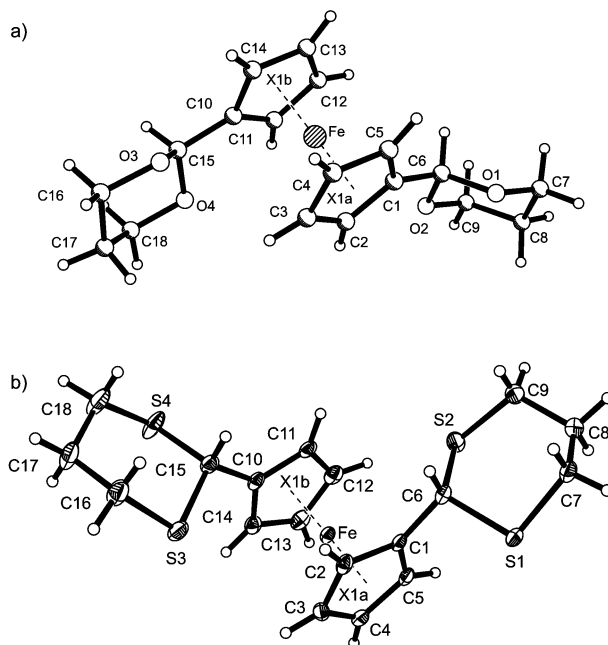


Fig. 2 The molecular structures of the analogous compounds **1** (a) and **6** (b). The displacement ellipsoids for **6** are drawn at 50% probability level.

from these planes respectively by –0.660 and 0.634 Å in **1**, and –0.881 and 0.696 Å in **6**. The gas phase electron diffraction study of underivatized dithiane²⁴ also showed the chair conformation and bond lengths [average C–S 1.812(3) and C–C 1.533(2) Å] comparable to those observed in **6** (see Table 3). Compounds **1** and **6** differ substantially by orientation of dioxane and dithiane rings with respect to the Cp rings. The corresponding dithiane rings in **6** approach a perpendicular (with respect to Cp rings) orientation. The angle between the mean planes of S1, S2, C7, C9 and Cp plane is 99° and that between the two planes through S3, S4, C16, C18 and Cp is 108°. The corresponding dioxane rings in **1** approach a parallel orientation in respect to the corresponding Cp rings. The mean plane through O1, O2, C7, C9 and that through C1, C2, C3, C4, C5 form an angle of 35.9°, the angle between two planes through O3, O4, C16, C18 and C10, C11, C12, C13, C14 being of 7.9°.

The results of the X-ray diffraction study of **5a**, which crystallised as a pure enantiomer in the noncentrosymmetric *P*₂,*2*,*2* space group are summarized in Fig. 3. The atoms C7, C9 and C16, C18 possess respectively *S,R* and *S,R* absolute configurations. The ferrocene moiety showed the expected geometry with no unusual bond lengths or angles. The two Cp

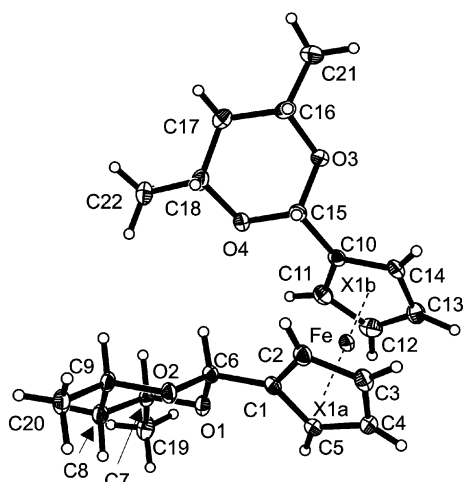


Fig. 3 The molecular structure of **5a**. The displacement ellipsoids are drawn at 50% probability level.

rings are almost parallel to each other with dihedral angle of 2.5° . The $\text{Cp} \cdots \text{Fe} \cdots \text{Cp}$ torsional twist angle is 56.6° corresponding to synclinal conformation. As for **6** and **1** both dioxane rings adopt a chair conformation with the Cp substituent in an equatorial orientation. The atoms O1, O2, C1, C7 and O3, O4, C16, C18 occupy coplanar positions within ± 0.005 and ± 0.003 Å correspondingly, with carbon atoms C6 and C8, C15 and C17 on opposite sides of the corresponding mean planes at -0.655 and 0.672 Å, 0.670 and -0.640 Å. The angle between the mean planes through O1, O2, C7, C9 and Cp plane is 42.1° and that through O3, O4, C16, C18 and Cp is 39.9° .

Unlike isomer **5a**, compound **5b** crystallised as a mixture of two stereoisomers A (63%) and B (37%), which differ by configurations at asymmetric centres C16 and C18 (Fig. 4). In the enantiomer **5bA** both atoms C16 and C18 have *S* configurations, whereas C16x and C18x possess *R* configurations (Fig. 5). The Cp rings are nearly parallel to each other, the dihedral angle being at 1.5° . The $\text{Cp} \cdots \text{Fe} \cdots \text{Cp}$ torsional twist angle is 62.2° corresponding to a synclinal conformation. The dioxane rings in both isomers adopt a chair conformation with the Cp substituent in an equatorial orientation. The arrangement of these two dioxane rings with respect to the Cp rings is different. The dioxane attached to C1 makes a dihedral angle of 44.7° with the corresponding Cp ring, whereas the other dioxane rings coupled at C10 form with Cp dihedral angles of 115.2 and 130.7° for A and B respectively.

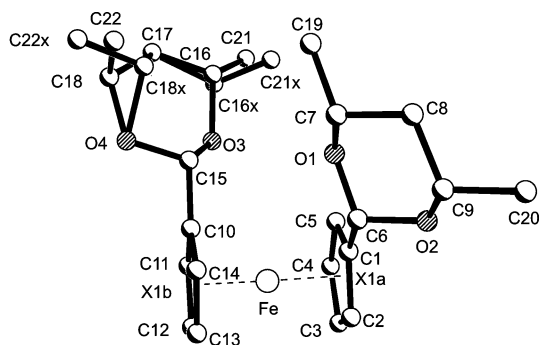


Fig. 4 The molecular structure of **5b** showing the presence of two stereoisomers (63 : 37) in one of the 4,6-dimethyl-1,3-dioxane rings. H-atoms are omitted for clarity.

Mass spectrometry investigations

The binding behaviour of compounds **1** and **6** toward hard alkali (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and soft transition metal cations (Zn^{2+} , Ag^+ , Hg^{2+}) was studied by ESI-MS (for calculated m/z ratios of the ligands as well as of the adducts see Table 4). The compounds have similar geometry but different donor

Table 4 List of the calculated m/z ratios for the ligands and for the expected interactions with metal ions

Compound	Formula	m/z ratio
1	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{H}]^+$	359
1 + LiCl	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Li}]^+$	365
1 + NaCl	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Na}]^+$	381
1 + KCl	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{K}]^+$	397
1 + RbCl	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Rb}]^+$	443
1 + CsCl	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Cs}]^+$	491
1 + ZnCl_2	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{ZnCl}]^+$	457
1 + AgNO_3	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Ag}]^+$	465
1 + HgCl_2	$[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{HgCl}]^+$	595
6	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{H}]^+$	423
6 + LiCl	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Li}]^+$	429
6 + NaCl	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Na}]^+$	445
6 + KCl	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{K}]^+$	461
6 + RbCl	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Rb}]^+$	507
6 + CsCl	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Cs}]^+$	555
6 + ZnCl_2	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{ZnCl}]^+$	523
6 + AgNO_3	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Ag}]^+$	531
6 + HgCl_2	$[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{HgCl}]^+$	659

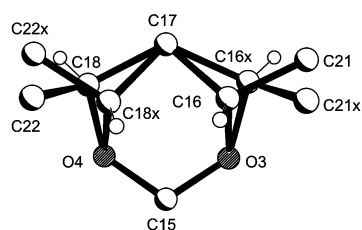


Fig. 5 The 4,6-dimethyl-1,3-dioxane ring in **5b**.

atoms. Compound **1** contains hard ether oxygen donors, whereas **6** involves soft sulfur atoms.

Compound **1** showed under competitive conditions in the presence of equal concentrations of the whole set of alkali metal ions, as expected, binding preference toward Li^+ and Na^+ . When, however, the 1 : 1 mixture of **1** and Na^+ in the presence of 10-fold excess of Li^+ , K^+ , Rb^+ , and Cs^+ was investigated, the most abundant peak was observed at m/z 365, corresponding to $[\text{C}_{18}\text{H}_{22}\text{FeO}_4 + \text{Li}]^+$. In the presence of a 10-fold excess of Na^+ , K^+ , Rb^+ , and Cs^+ over Li^+ **1** showed the highest affinity toward Na^+ . This indicates that **1** has close affinity to both Li^+ and Na^+ , which is superior to that with respect to K^+ , Rb^+ , and Cs^+ (see Fig. 6).

Compound **6** revealed low affinity toward Li^+ and Na^+ and high binding preference for alkali metal ions with large ion radii

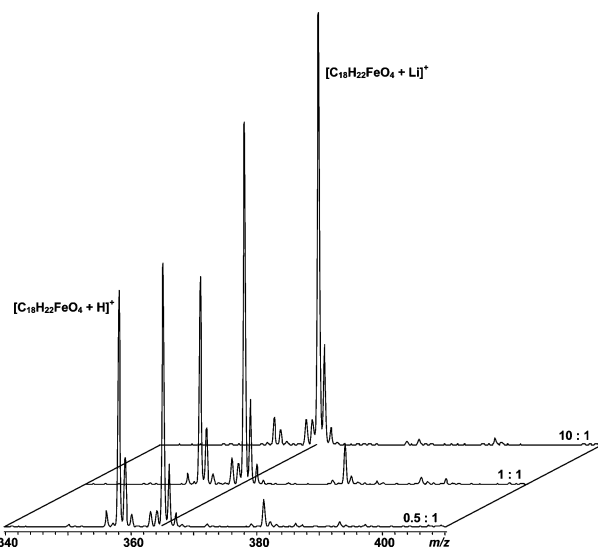


Fig. 6 Mass spectra for the reaction between Li^+ and **1** at ratios of 0.5 : 1, 1 : 1, and 10 : 1.

(for the ion radii of the cations see ref. 25). As expected, the most intense peak was observed at m/z 555, attributable to $[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{Cs}]^+$. The high affinity of **6** for Cs^+ has also been confirmed when the reaction was carried out in the presence of a 10-fold excess of Li^+ , Na^+ , K^+ , and Rb^+ over Cs^+ . The peak at m/z 555 was the most intense in the mass spectrum.

According to the HSAB principle we did not expect to observe high affinity of transition metal ions Zn^{2+} , Ag^+ , or Hg^{2+} toward the dioxane-based species **1**, as it was indeed the case in our mass spectrometry experiments. Only peaks of marginal intensity were registered in the mass spectra. The isotopic patterns indicated the presence of transition metal ions in the adducts formed. In all experiments the protonated ligand peak was found to be the most abundant.

In contrast, the formation of stable associates was expected between **6** and Zn^{2+} , Ag^+ , and Hg^{2+} . While only moderate affinity toward Zn^{2+} was observed, the binding preference for Hg^{2+} and Ag^+ was evident. Competitive experiments demonstrated the higher preference of the dithiane rings toward Hg^{2+} than for Ag^+ , even in the presence of a 10-fold excess of Zn^{2+} and Ag^+ . The peak at m/z 659 corresponding to $[\text{C}_{18}\text{H}_{22}\text{FeS}_4 + \text{HgCl}]^+$ was found to be the most intense in the mass spectrum.

4 Conclusions

In this report the synthesis of new ferrocene derivatives by a straightforward, one step-one pot condensation is presented. We succeeded in obtaining four single crystals suitable for X-ray diffraction analyses – two different diastereomers were obtained after separation of the reaction mixture of 1,1'-diformylferrocene and 2,4-pentanediol by column chromatography. ESI-MS investigations on the binding behaviour of 1,1'-bis(1,3-dioxane-2-yl)ferrocene **1** and 1,1'-bis(1,3-dithiane-2-yl)ferrocene **6** toward selected alkali and transition metal cations revealed affinity of **1** toward Li^+ and Na^+ , while the preference of **6** toward Hg^{2+} was expectable.

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