Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Organometallic Chemistry 689 (2004) 2250–2255

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Electronic communication through the ureylene bridge: spectroscopy, structure and electrochemistry of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) ☆

Khaled Mahmoud [a], Yi-Tao Long [a], Gabriele Schatte [b], Heinz-Bernhard Kraatz [a,*]

[a] *Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK, Canada S7N 5C9*
[b] *Saskatchewan Structural Science Centre, University of Saskatchewan, Saskatoon, SK, Canada S7N 5C9*

Received 8 March 2004; accepted 8 April 2004

Abstract

Dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) formed during the synthesis of 1-amino, 1′-ferrocenecarboxylic acid shows virtual molecular centrosymmetry. Electronic coupling between the two Fc groups through the ureylene bridge results in both Fc groups being individually oxidizable ($\Delta E_{1/2} \gg 0.14$ V). The possible existence of intermolecular electronic communication has discussed. The oxidation was followed by spectroelectrochemistry. The separation between the two halfwave potentials $\Delta E_{1/2} = 137 \pm 5$ mV and the comproportionation constant $K_c = 207$.

Keywords: Electronic communication; Diferrocene; Spectroelectrochemistry; Ureylene bridge

1. Introduction

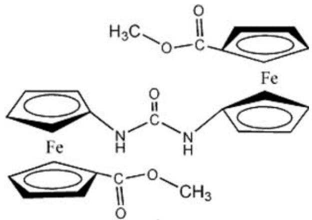
The chemistry of chemically linked redox groups, such as ferrocene, has received significant attention [1]. In general, molecules having multiple redox sites can exhibit a single redox event if the redox active sites are electronically isolated. If coupling exists between the redox sites, the oxidation of one site influences the other redox site and shifts its potential [2]. The separation between the redox potentials of two redox sites present in a molecule is routinely seen as a guide to the magnitude of the intramolecular electronic communication [3]. In some cases, the electronic interaction between the redox centers can be very small such as for 1,4-tetrafluorophenylene-linked ferrocenes, for which the Osteryoung square wave voltammogram shows only a broadening of the redox wave rather than a splitting [4]. Recent examples of investigations into the electronic communication include the study of a series of unsymmetrically substituted 1,1′-ferrocenyldisulfides [5], which belong to the partially delocalized Robin–Day II class [6]. Methylene-bridged diferrocenyl fullerenes exhibit a weak electronic interaction causing cathodic shifts of the C_{60}-based reduction waves [7]. Hafner and coworkers [8] recently reported that a butadiynyl bridged ferrocenophane in which the two Fc groups exhibit two separate one-electron oxidations with a large separation between the two halfwave potentials $\Delta E_{1/2}$ of 250 mV indicating electronic coupling over 8.025(5) Å between the two iron centers through the alkyne bridge. Other linked diferrocenes also often display a significant amount of electronic interactions between the ferrocene systems through the spacer molecule [9]. The electrochemical behavior of ferrocenes linked to tetrathiofulvalene (TTF) shows the redox characteristics of the constituents, showing an oxidation from the neutral Fc-TTF to a dicationic Fc-exTTF^{2+} and finally to tricationic Fc^{+}-exTTF^{2+} in two separate steps [10]. The redox behavior of some 1,4-bis(ferrocenyl)butadiyne coordinated osmium clusters containing two bridged ferrocenyl moieties suggested a significant electronic communication between them [11].

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.04.016.

[*] Corresponding author. Tel.: +1306-966-4660; fax: +1306-966-4730.
E-mail address: kraatz@skyway.usask.ca (H.-B. Kraatz).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.04.016

Rapic and coworkers [12] recently described the efficient synthesis of 1-amino,1′-ferrocenecarboxylic acid ($(H_2N–C_5H_4)Fe(C_5H_4COOH)$). During the synthesis the symmetrical ferrocenyl-substituted urea, dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) was formed as a by-product. This compound is of fundamental interest since the ureylene bridge may allow for the electronic communication between the two ferrocene groups, which may make this an interesting compound for the design of circuit components in molecular electronics.



1

In this paper, we report the results of a combined crystallographic and electrochemical investigation of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) in which two ferrocene groups are linked through a urea linkage –NH–C(O)–NH– and show that the two ferrocene groups in are electronically in communication through the urea bridge.

2. Experimental

2.1. General procedure

1′-azidocarbonylferrocene-1-metylcarboxylate was obtained according to the literature procedure [12]. For column chromatography, a column with a width of 2.7 cm (ID) and a length of 45 cm was packed 18–22 cm high with 230–400 mesh silica gel (VWR). For TLC, aluminum plates coated with silica gel 60 F_{254} (EM Science) were used. NMR spectra were recorded on a Bruker AMX-500 spectrometer operating at 500.230 MHz (^1H) and 125.783 MHz ($^{13}C\{^1H\}$). Peak positions in both ^1H and ^{13}C spectra are reported in ppm relative to TMS. The ^1H NMR spectra are referenced to the residual $CHCl_3$ signal at $\delta 7.27$. All $^{13}C\{^1H\}$ spectra are referenced to the $CDCl_3$ signal at $\delta 77.23$ ppm. Mass spectrometry was carried out on a VG Analytical 70/20 VSE instrument. Infrared spectra were obtained with a Perkin–Elmer model 1605 FT-IR

2.2. Preparation of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (1)

The preparation of the title compound follows that reported by Rapic and coworkers [12]. On refluxing a solution of 1′-azidocarbonylferrocene-1-metylcarboxylate (600 mg, 2 mmol) for 6 h in dry *tert*-butyl alcohol (25 ml) and evaporation to dryness, purification was carried out by flash column chromatography ($EtOAc:CH_2Cl_2$, 1:9). The first fraction was *tert*-butyl-1′-methoxycarbonyl-1-ferrocenecarbamate (366 mg, 60%; $R_f = 0.86$) which was followed by the deep orange title compound dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**). ($R_f = 0.34$). Yield: 89 mg, 9%. M.p. 159.5–160 °C (lit. 160–160.5 °C). FAB-MS (*m/z*). Calc. for $C_{25}H_{25}N_2O_5Fe_2$ $[M+1]^+$: 544.17. Found: 544.04. FT-IR (KBr, cm^{-1}): 3377 (m, N-H), 1699 (s, C=O, $COOCH_3$ and NHCONH). UV–vis (MeCN; λ in nm (ε in $L\,mol^{-1}\,cm^{-1}$)): 447 (607). ^1H NMR (DMSO, δ/ppm): 7.70 (1H, bs, NH), 4.70 (2H, s, H-2 and H-5, Fn), 4.58 (2H, s, H-2′ and H-5′, Fc), 4.42 (2H, s, H-3 H-4, Fc), 3.98 (2 H, s, H-3′ and H-4′, Fc), 3.67 (3H, s, Me). ^{13}C NMR, (DMSO, δ/ppm): 170.5 (*C*OOCH3), 152.8 (NH*C*ONH), 100.2 (C-1′, Fc), 73.0 (C-2, C-5, Fc), 72.4 (C-1, Fc), 71.2 (C-2′ and C-5′, Fc), 65.9 (C-3 and C-4, Fc), 61.4 (C-3′ and C-4′, Fc), 52.2 (COO*C*H3).

2.3. Electrochemical measurements

The electrochemical experiments were carried out at room temperature using CV-50W voltammetric analyzer. A gold electrode (diameter 50 μm) was used as working electrodes. A solution of 5 mM of the Sym. Urea compound was prepared in MeCN as solvent, 0.1 M tetrabutylammonium perchlorate(TBAP) was the supporting electrolyte. The sensitivity was 100 μA for the gold electrode. The measurements carried out in a low scan rate of 100, 10 mV/s for cyclic voltammetry and square wave voltammetry, respectively. A platinum wire (1 mm) and commercial Ag/AgCl (BAS) being the counter and the reference electrodes, respectively. The potential value of the ferrocene/ferrocenium couple under the present experimental conditions $E_{1/2} = 448(\pm 5)$.

Spectroelectrochemical experiments were performed in a thin layer quartz cell (path length 0.3 mm, volume 120 μL) containing a Pt mesh electrode (Alfa Aesar, MA, USA, 99.9%, 52 mesh, open area 63%, wire diameter = 0.10 mm), a Pt counter wire and a Ag/AgCl quasi-reference electrode. 120 μL of a 5 mM dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) solution in CH_3CN containing 0.1 M tetrabutylammonium perchlorate (TBAP) was injected into the cell immediately before measurements. The mesh electrode was aligned such that the UV–vis beam (Cary 500, Varian) passed through the centre of the working electrode. Potentials were controlled by the CHI660 electrochemical workstation (CH Instruments, USA).

2.4. X-ray crystallography

Suitable crystals of compounds **1** (dark orange needles; 0.40 × 0.10 × 0.10 mm) were obtained from a ether-layered solution of the compounds in chloroform. All measurements were made on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at −100 °C. An initial orientation matrix and cell was determined from 10 frames using ϕ-scans (1° per frame, 20 s exposures per degree for a 10° rotation). Data were measured using ϕ- and ω-scans [13a]. Data reduction was performed with the HKL DENZO and SCALEPACK software [13b]. The structure was solved using direct methods [13c]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C–H bond distances 0.95/0.99 Å; N–H bond distance 0.88 Å) and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon or nitrogen atom. The hydrogen atom at the $CHCl_3$ molecule was located in Fourier difference map. Its coordinates were allowed to refine, whereas its isotropic thermal parameter was fixed at 1.2 times that of the preceding carbon atom. The final cycle of full-matrix least squares refinement using F^2 (SHELXL97-2) [13d] was based on 6238 reflections, 348 variable parameters and converged with $R_1 = 0.0375$ for $I > 2\sigma(I)$. Crystallographic details for **1** are found in Table 1. CCDC reference numbers 232587 (Compound **1**).

Table 1
Crystal data and structure refinement for dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) ($CHCl_3$ solvate)

Empirical formula	$C_{26}H_{25}Cl_3Fe_2N_2O_5$
Formula weight	663.53
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	
a (Å)	11.2400(2)
b (Å)	11.9210(2)
c (Å)	19.5200(4)
β (°)	94.1340(8)
V (Å^3)	2608.72(8)
Z	4
D_{calc} (g/m^3)	1.689
Absorption coefficient (mm^{-1})	1.461
$F(000)$	1352
Crystal size (mm)	0.40 × 0.10 × 0.10
θ Range for data collection	1.00–27.88°
Limiting indices	$-14 < h < 14, -14 < k < 15, -25 < l < 25$
Reflections collected	11966
Independent reflections	6238
Data/restraints/parameters	6238/0/348
Goodness-of-fit (F^2)	1.030
$R_1[I > 2\sigma(I)]$[a]	$R_1 = 0.0375$
wR_2 (all data)[b]	$wR_2 = 0.0921$

[a] $R_1 = [\sum |F_o| - |F_c||]/[\sum |F_o|]$ for $[I > 2\sigma(I)]$.

[b] $wR_2 = \left\{\left[\sum w(F_o^2 - F_c^2)^2\right]\Big/\left[\sum w(F_o^2)^2\right]\right\}^{1/2}$ (all data).

3. Results and discussion

The synthesis of the symmetrical urea is analogous to that described by Rapic and coworkers [12]. The ^1H and ^{13}C NMR spectra both show the compound to be centrosymmetric, giving four signals for protons of the four inequivalent protons of the disubstituted Fc group. The ester C═O shows a signal at δ170.5, while that of the urea C is observed further upfield at δ152.8. The compound exhibits a strong absorption band in the visible region with a $\lambda_{max} = 447$ nm, typical of the d–d transition in ferrocene derivatives.

The IR shows a single broad signal at 3377 cm^{-1} due to the NH stretch. The C═O stretching vibrations of the ester and the urea are not resolved but give a single strong peak at 1699 cm^{-1}. The material crystallized readily from ether-layered chloroform giving dark orange needles, which were of sufficiently high quality to carry out a single crystal X-ray study of compound **1**. Its structure together with selected bond angles and distances are given in Fig. 1. The structure of compound **1** crystallizes in the centrosymmetric space group $P2_1/a$. The molecule is almost centrosymmetric, as expected based on the spectroscopic information. The Cp planes are virtually coplanar with respect to the urea plane, with dihedral angles close to 180° (C(10)–N(11)–C(15)–N(12) = −174.44(19)° and C(30)–N(12)–C(15)–N(11) = −177.47(19)°), which should allow for good overlap of the π-systems of the urea bridge and the two ferrocene groups. The structure of several *N*,*N*′-substituted ureas was reported in the literature [14].

In general, these systems exhibit two *trans* amide bonds, which leads to both N–H bonds pointing towards the same direction whereas the carbonyl C═O points to the opposite direction. This facilitates self-complementary bi-directional H-bonding leading to the formation of a supramolecular H-bonded structure. For example, dimethyl 4.4′-ureylenedibutyrate and the diglycine urea derivative engage in intermolecular H-bonding interactions involving the central urea core, having the C═O interacting with the two N–H groups of an neighboring molecule. H-bonding distances in these compounds are longer than that found in compound **1** (see below), whereas those found in the butyrate are 2.916 (5) and 2.918 (5) Å. For the diglycine system a H-bonding distance of 2.916 (7) Å was reported [15] Guichard and coworkers [16] reported H-bonded distances ranging from 2.83 to 3.27 Å for a leucine–urea derivative. The H-bonding interactions in this urea are fundamentally different. The urea carbonyl is not engaging in H-bonding interactions and resulting in a short C═O bond of 1.217(3) Å. The H-bonded urea C═O described cited above exhibit C═O distances that are clearly elongated due to its involvement in H-bonding. The compound engages in intermolecular H-bonding involving interactions between the methylester substitutent of one Cp

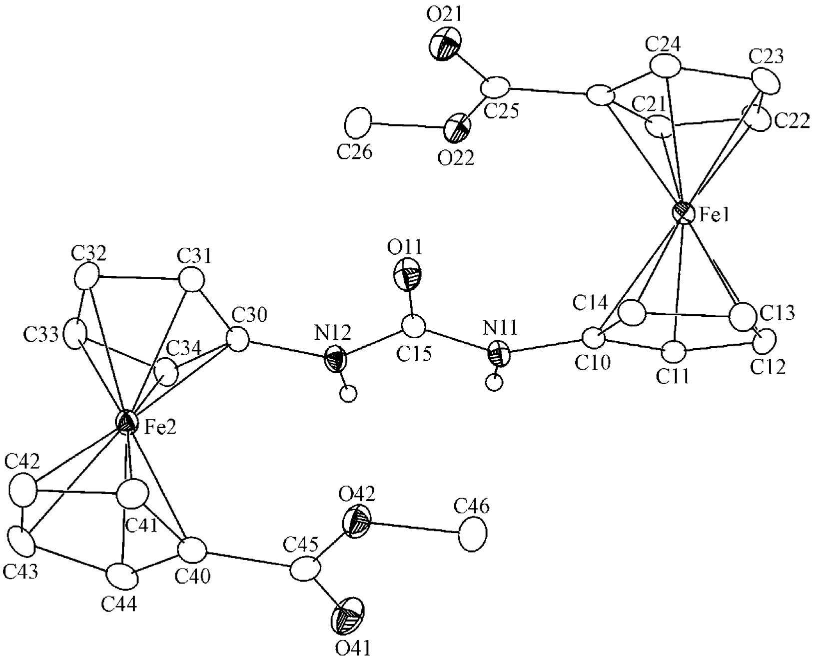


Fig. 1. ORTEP of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**). The solvent is omitted for clarity. Selected bond distances and angles: Fe(1)–ct(Cp1) = 1.664(1), Fe(1)–ct(Cp2) = 1.652(1), Fe(2)–ct(Cp3) = 1.663(1), Fe(2)–ct(Cp4) = 1.653(1), N(11)–C(10) = 1.395(3), N(11)–C(15) = 1.367(3), N(12)–C(15) = 1.378(3), N(12)–C(30) = 1.404(3), O(11)–C(15) = 1.217(3) Å; C(15)–N(11)–C(10) = 125.20(19)°, C(15)–N(12)–C(30) = 124.85(19)°, O(11)–C(15)–N(11) = 123.6(2)°, O(11)–C(15)–N(12) = 124.0(2)°, N(11)–C(15)–N(12) = 112.4(2)°.

ring to the urea N–H of an adjacent molecule ((N(11)$\cdots$O(21)*) = 2.819(3) Å).

In terms of the supramolecular structure, this results in the formation of a one-dimensional chain. However, on the molecular level, this introduces a degree of asymmetry in the molecule which manifests itself in two different C–N bond lengths (N(11)–C(15) = 1.367(3), N(12)–C(15) = 1.378(3) Å). The C–N bond of the nitrogen involved in H-binding is significantly shortened compared to the one that is not involved in H-binding. This new H-bonding motif is interesting. We suggest that the position of the solvent molecule interferes with the symmetric H-bonding found between the methylester C=O and the urea N–H of an adjacent molecule (Fig. 2).

Next we carried out cyclic voltammetry (CV) and square wave voltammetry (SWV) in order to investigate its electrochemical properties. As shown in Fig. 3, the two, likely ferrocene-centered, oxidation display chemical reversibility in the cyclic voltammetric time scale at halfwave potentials $E_{1/2}$ of 422 ± 5 and at 559 ± 5 mV (vs. Ag/AgCl). The first oxidation wave corresponds to the oxidation of one of the two Fc groups resulting in the formation of the monocationic mixed valance species. At higher potential the second Fc group is oxidized giving the dicationic complex. The square wave voltammetry (Fig. 3(b)) shows clearly the separation between the two oxidation peaks. The difference between the two redox events $\Delta E_{1/2}$ is 137 ± 5 mV.

From this, a comproportionation constant K_c can be derived according to $K_c = 10^{16.9\Delta E_{1/2}}$, with $\Delta E_{1/2}$ in V, which gives $K_c = 207$. As a general guide, the larger $\Delta E_{1/2}$ and K_c of linked redox systems are, the higher the extent of the electronic interaction between the two redox sites. According to this, the molecule $\mathbf{1}^+$ can be categorized as Robin–Day class II cation, in which the urea bridge allows for significant electronic interactions between the two Fc groups [6]. However, recently it was demonstrated that the solvent and the counter ion in the electrochemical experiment plays an important role [17].

In situ spectroelectrochemistry allows the simultaneous detecting of electrochemical and spectral characterization in the UV/vis-NIR regions. Fig. 4 shows a series of UV/vis-NIR absorbance spectra obtained during the electrochemical oxidation of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**). In the initial spectrum, the peak at 447 nm is assigned to the d–d transition of the ferrocene moieties.

While applying a potential of 500 mV (vs. Ag/AgCl), the potential at which the first Fc oxidation is observed to give $\mathbf{1}^+$, the absorbance at 447 nm is gradually blue shifted to 411 nm with time and a new peak at 890 nm appeared, which most likely belongs to the mixed valence Fe(II)/Fe(III) species. As the potential is increased to 550 mV, the second Fc group begins to oxidize to give $\mathbf{1}^{2+}$. As a consequence, the low energy absorbance at 890 nm disappeared. Applying a potential of 800 mV resulted in

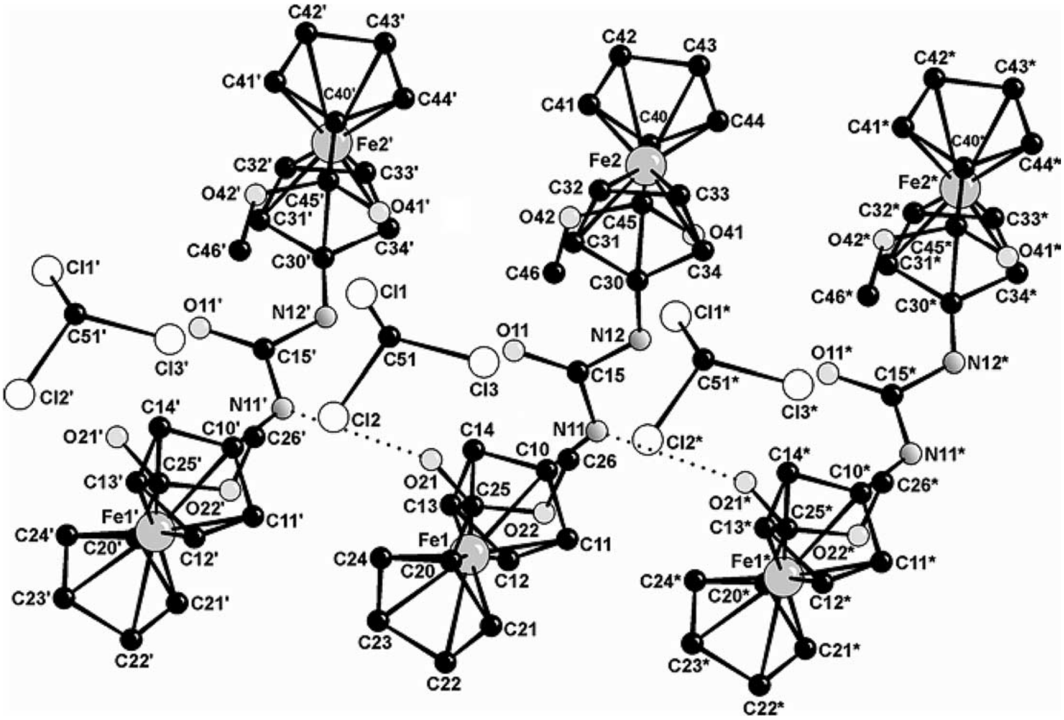


Fig. 2. Plot of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) showing the intermolecular H-bonding interactions between the methylester C=O and the urea N–H of an adjacent molecule resulting in a slight asymmetry of the urea group. The solvent molecule $CHCl_3$ is included in the plot.

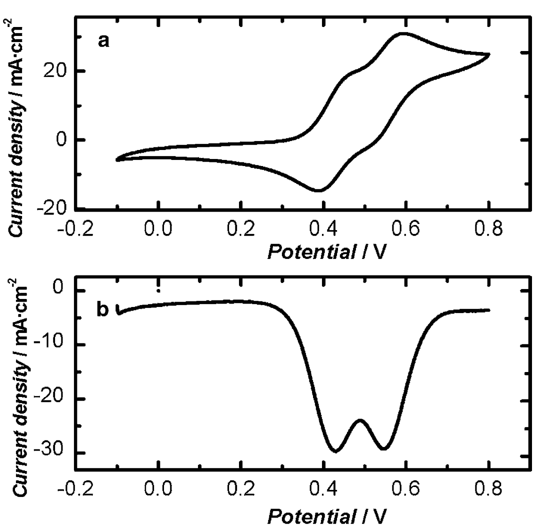


Fig. 3. Electrochemical study of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) (**1**) in CH_3CN/0.1 M TBAP: (a) shows the cyclic voltammetry at a scan rate of 100 mV/s; (b) shows the square wave voltammetry at a scan rate 10 mV/s.

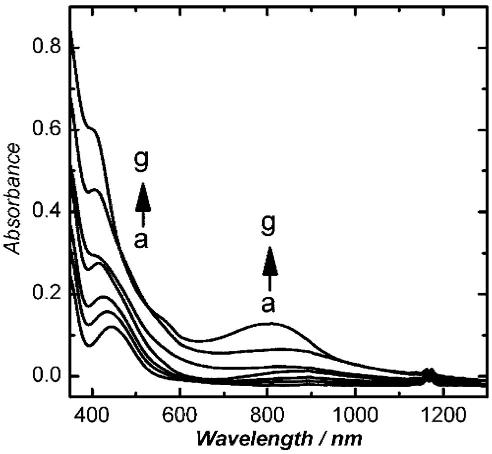


Fig. 4. Spectroelectrochemical follow up of the oxidation of dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate) in CH_3CN/0.1 M TBAP: (a) open circuit potential; (b) 550 mV, 3 min; (c) 550 mV, 6 min; (d) 550 mV, 9 min; (e) 800 mV, 3 min; (f) 800 mV 6 min; (g), 800 mV, 9 min.

the complete oxidation of **1** in the thin-layer cell to give $\mathbf{1}^{2+}$ and the appearance of a peak at 800 nm. Importantly, these changes are fully reversible. Thus, upon stepping the potential to −0.300 V (vs. Ag/AgCl) causes reduction back from the dication to the neutral complex **1**, and the spectrum showed only the original peak at $\lambda_{\max} = 477$ nm.

4. Summary

In the solid state, dimethyl 1′,1′-ureylenedi(1-ferrocenecarboxylate), first reported by Rapic as a side product in the synthesis of 1-amino,1′-ferrocenecarboxylic acid, exhibits coplanarity of the ureylene bridge and the two Fc groups allowing for some electronic coupling the two redox centers. Electronic communication through the ureylene bridge results in the two separate redox waves for the two redox centers with a moderate separation between the two $E_{1/2}$, rendering $\mathbf{1}^+$ a class II complex according to the Robin–Day classification. We are now exploring the switching properties of substituted diferrocene derivatives on surfaces.

Acknowledgements

Financial support from NSERC, CFI and SIF is gratefully acknowledged. H.-B.K. is the Canada Research Chair in Biomaterials. We are grateful to the Saskatchewan Structure Science Center (SSSC) for providing access to all necessary instrumentation. Ken Thoms, Chemistry Department, University of Saskatchewan, is also acknowledged for carrying out the MS experiments.

References

[1] (a) F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J.-l. Fillaut, M.-H. Delville, D. Astruc, Angew. Chem., Int. Ed. Engl. 32 (1993) 1075;
(b) D.M. Duggan, D.N. Hendrickson, Inorg. Chem. 14 (1975) 955;
(c) A. Togni, M. Hobi, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, Organometallics 13 (1994) 1224;
(d) L.M. Tolbert, X. Zhao, Y. Ding, L.A. Bottomley, J. Am. Chem. Soc. 117 (1995) 12891;
(e) D. Astruc, New J. Chem. 16 (1992) 305.

[2] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, Chem. Rev. 101 (2001) 2655.

[3] D.E. Richardson, H. Taube, Inorg. Chem. 20 (1981) 1278.

[4] P.A. Deck, M.J. Lane, J.L. Montgomery, C. Slebodnick, F.R. Fronczek, Organometallics 19 (2000) 1013.

[5] V.C. Gibson, N.J. Long, R.J. Long, A.J.P. White, C.K. Williams, D.J. Williams, E. Grigiotti, P. Zanello, Organometallics 23 (2004) 957.

[6] M.D. Robin, P. Day, Adv. Inorg. Chem. Radiochem. 10 (1967) 247.

[7] K.-Y. Kay, L.H. Kim, I.C. Oh, Tetrahedron Lett. 41 (2000) 1397.

[8] K.H.H. Fabian, H.-J. Lindner, N. Nimmerfroh, K. Hafner, Angew. Chem. Int. Ed. 40 (2001) 3402.

[9] (a) A.J. Moore, M.R. Bryce, P.J. Skabara, A.S. Batsanov, L.M. Goldenberg, J.A.K. Howard, J. Chem. Soc. Perkin Trans. 1 (1997) 3443;
(b) A.A.O. Sarhan, T. Izumi, J. Organomet. Chem. 675 (2003) 1;
(c) S.L. Guo, F. Peters, F. Fabrizi de Biani, J.W. Bats, E. Herdtweck, P. Zanello, M. Wagner, Inorg. Chem. 40 (2001) 4928;
(d) K. Ma, F. Fabrizi de Biani, M. Bolte, P. Zanello, M. Wagner, Organometallics 21 (2002) 3979;
(e) W. Skibar, H. Kopacka, K. Wurst, C. Salzmann, K.-H. Ongania, F. Fabrizi de Biani, P. Zanello, B. Bildstein, Organometallics 23 (2004) 1024;
(f) T.-Y. Dong, P.-H. Ho, X.-Q. Lai, Z.-W. Lin, K.-J. Lin, Organometallics 19 (2000) 1096;
(g) L.M. Tolbert, X. Zhao, Y. Ding, L.A. Bottomley, J. Am. Chem. Soc. 117 (1995) 12891;
(h) S. Barlow, L.M. Henling, M.W. Day, W.P. Schaefer, J.C. Green, T. Hascall, S.R. Marder, J. Am. Chem. Soc. 124 (2002) 6285;
(i) C. Engtrakul, L.R. Sita, Nano Lett. 1 (2001) 541;
(j) A. Tarraga, P. Molina, D. Curiel, M.D. Velasco, Organometallics 20 (2001) 2125;
(k) K.R.J. Thomas, J.T. Lin, Y.S. Wen, Organometallics 19 (2000) 1008.

[10] S.-G. Liu, I. Perez, N. Martin, L. Echegoyen, J. Org. Chem. 65 (2000) 9092.

[11] (a) R.D. Adams, B. Qu, M.D. Smith, T.A. Albright, Organometallics 21 (2002) 2970;
(b) R.D. Adams, B. Qu, Organometallics 19 (2002) 2411.

[12] L. Barisic, V. Rapic, V. Kovac, Croat. Chem. Acta 75 (2002) 199.

[13] (a) COLLECT data collection software, Nonius B.V., 1998;
(b) HKL DENZO and SCALEPACK v1.96 : Z. Otwinowski, W. Minor, in: C.W. Carter, Jr., R.M. Sweet (Eds.), Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology, Macromolecular Crystallography, Part A, Academic Press, San Diego, CA, 1997, vol. 276, pp. 307–326
(c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, M.C. Burla, G. Polidori, M. Camalli, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115;
(d) G.M. Sheldrick, SHELXL97-2, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

[14] (a) V. Coiro, P. Giacomello, E. Giglio, Acta Crystallogr. B 27 (1971) 2112;
(b) W. Dannecker, J. Kopf, H. Rust, Cryst. Struct. Commun. 8 (1979) 429.

[15] X. Zhao, Y.-L. Chang, F.W. Fowler, J.W. Lauher, J. Am. Chem. Soc. 112 (1990) 6627.

[16] V. Semetey, C. Hemmerlin, C. Didierjean, A.-P. Schaffner, A. Gimenez Giner, A. Aubry, J.-P. Briand, M. Marraud, G. Guichard, Org. Lett. 3 (2001) 3843.

[17] F. Barriere, N. Camire, W.E. Geiger, U.T. Mueller-Westerhoff, R. Sanders, J. Am. Chem. Soc. 124 (2002) 7262.