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Photochemical reaction of (η^5-cyclopentadienyl) dicarbonyliron iodide with 1-substituted uracils in the presence of diisopropylamine: crystal structure of the (η^5-C_5H_5) Fe(CO) $_2$ complex of deprotonated 5-fluoro-1-(tetrahydro-2-furyl) uracil (Ftorafur)

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Abstract

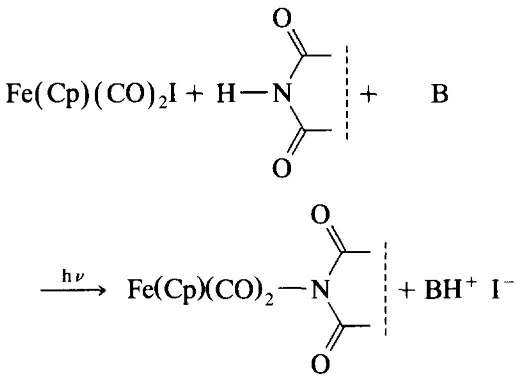
Irradiation with visible light of a mixture of Fe(Cp)(CO)$_2$I (Cp = η^5-cyclopentadienyl) with 1-methyluracil (**1a**), 5-fluoro-1-(tetrahydro-2-furyl)uracil (Ftorafur) (**1b**) or 6-azauridine-2′3′5′-triacetate (**1c**) in the presence of diisopropylamine affords complexes in which the Fe(Cp)(CO)$_2$ moiety is bound to the deprotonated N(3) atom of the uracil moiety. The crystal structure of **2b**, made from **1b**, was determined and is compared with the known structures of the α_A, α_B and β forms of Ftorafur and that of its η^1-Au complex. Complex **2b** shows the shortest intramolecular C–H ··· O hydrogen bond between the tetrahydrofuran and uracil rings. The stereochemistry of this complex is also discussed.

Keywords: Iron; Carbonyl; Cyclopentadienyl; Uracils; Crystal structure

1. Introduction

Interactions of transition metal ions in inorganic complexes with nucleobases, nucleosides and nucleotides has been extensively studied [1]. In contrast, very little is known about organometallic complexes of these biologically important ligands [2], although such complexes could perhaps be useful as, for example, markers in immunoassays [3].

One of us recently developed a photochemical method for displacement of iodide in Fe(Cp)(CO)$_2$I (Cp = η^5 – C_5H_5) by N anions of cyclic imides [4]. It involves illumination with visible light of a mixture this complex and the N–H imide in the presence of diisopropylamine:



(1)

(B = diisopropylamine)

The η^1-*N* co-ordination of the imidato ligand was recently confirmed by an X-ray structure determination of the complex Fe(Cp)(CO)$_2$(η^1-*N*-phthalimidato) [5].

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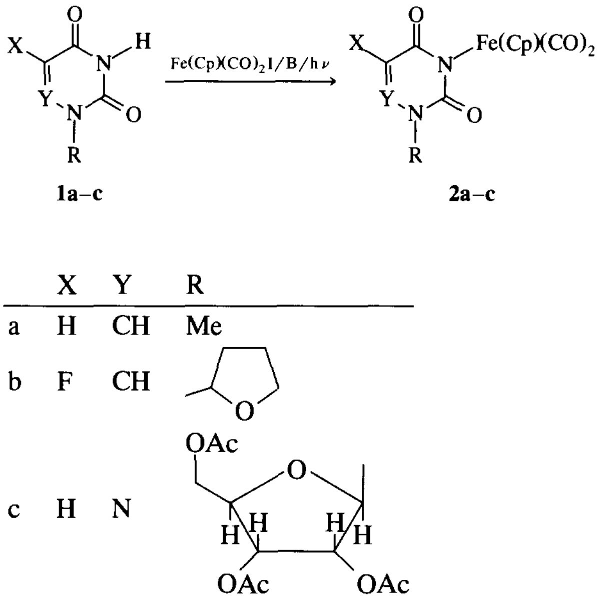
We report here that the reaction shown in Eq. (1) can be extended to some uracils and uracil nucleosides. Since the solvent of choice for this reaction is benzene or toluene, we had to use 1-substituted uracils that are soluble to some extent in these solvents. We investigated the simplest, 1-methyluracil (**1a**), and two more complex uracils, important in respect of their biological activity, these were 5-fluoro-1-(tetrahydro-2-furyl) uracil (**1b**) (a potent antitumor agent known as Ftorafur or Tegafur) [6] and an O-protected uracil nucleoside, 6-azauridine-2′3′5′-triacetate (**1c**). In order to establish the binding mode of the heterocyclic ligand and the influence of coordination on the ligand structure, the X-ray crystal structure of the Ftorafur complex was determined.

We hope that attachment of the Fe(Cp)(CO)$_2$ moiety to uracils may provide, for example, a method of labelling of these biologically important ligands for carbonylmetallimmunoassays [3]. On the contrary, coordination to iron can be expected to change the chemical reactivity of the heterocycle, making possible novel synthetic processes. (Uracils are useful starting materials in heterocyclic synthesis [7].)

2. Results and discussion

Irradiation with visible light of a mixture of Fe(Cp)(CO)$_2$I, a uracil **1a**–**1c** and diisopropylamine in benzene under argon gives the yellow air-stable complexes **2a**–**2c**:

Control experiments have shown that **2a**–**2c** are not formed in the dark. We assume that photosubstitution of iodide in Fe(Cp)(CO)$_2$I by the anions of **1a**–**1c** proceeds via photodissociation of CO, as suggested earlier for halide exchange [8]. However, the possibility of a photoassisted S$_N$2-type mechanism cannot be excluded.



1a–c **2a–c** (2)

When a stoichiometric amount of Fe(Cp)(CO)$_2$I was used, the reaction did not go to completion, and we obtained, together with the unchanged iodo complex, the products **2a**–**2c** contaminated with 10–15% of the corresponding uracils **1a**–**1c**. Purification of such products proved difficult, and longer photolysis times did not lead to greater purity. Consequently, we used an excess of Fe(Cp)(CO)$_2$I (about 2.5-fold) since this complex can be easily separated from **2a**–**2c** and under

Table 1
IR and ^{1}H NMR data for **2a**–**2c** and the corresponding N–H uracils

Compound	IR [a] (cm^{-1})		^{1}H NMR [b], δ (ppm)		
	ν(C≡O)	ν(C=O) (imide)	H(5)	H(6)	Others
2a	2050, 2000	1650, 1575	5.35 (d, $J(^1H-^1H) = 7.3$ Hz)	7.32 (d, $J(^1H-^1H) = 7.3$ Hz)	5.16 (s, Cp), 3.20 (s, Me)
1-methyl-uracil	—	1720, 1695	5.51 (d, $J(^1H-^1H) = 78$ Hz)	7.61 (d, $J(^1H-^1H) = 7.8$ Hz)	11.2 (br, NH), 3.22 (s, Me)
2b	2050, 2005	1655, 1590	—	7.50 (d, $J(^{19}F-H) = 7.0$ Hz)	5.92 (m), 5.22 (s, Cp), 4.18 (dd), 3.76 (dd), 2.3–1.8 (m)
Ftorafur	—	1710, 1690	—	7.87 (d, $J(^{19}F-H) = 7.0$ Hz)	5.87 (m), 4.22 (dd), 3.79 (dd), 2.4–1.8 (m)
2c	2055, 2005	1605, 1590	7.15 (s)	—	6.38 (d), 5.62 (dd), 5.46 (t), 5.06 (s, Cp), 4.4–4.0 (m), 2.10 (s), 2.08 (s), 2.07 (s)
6-azaur-idine-2′,3′,5′-triacetate	—	1705 [c]	7.51 (s)	—	9.4 (br, NH), 6.29 (d), 5.62 (dd), 5.41 (t), 4.4–4.0 (m), 2.11 (s), 2.08 (s), 2.07 (s)

[a] In CHCl$_3$ solutions.

[b] Solvent, (CD$_3$)$_2$SO (**2a** and **2b**, 1-methyluracil and florafur) or CDCl$_3$ (**2c** and 6-azauridine-2′,3′,5′-triacetate).

[c] Higher frequency signal obscured by the absorption of acetato groups.

Table 2
Isolated yields and analytical data for new complexes

Complex	Yield [a] (%)	Analysis [b] (%)		
		C	H	N
2a	91	48.0 (47.7)	3.4 (3.3)	9.35 (9.3)
2b	72	48.15 (47.9)	3.75 (3.5)	7.2 (7.45)
2c	51	46.2 (46.1)	3.8 (3.9)	7.45 (7.7)

[a] Based on the starting uracil.
[b] Required values given in parentheses.

these conditions the contamination of **1a–1c** in **2a–2c** was reduced to less than 0.5% (as indicated by ^{1}H NMR spectroscopy).

The complexes **2a–2c** were characterized by IR and ^{1}H NMR spectroscopy (Table 1) and by elemental analyses (Table 2). As expected for coordination through deprotonated N(3), on going from **1a–1c** to **2a–2c** there is an upfield shift (0.2–0.3 ppm) of the signals from the uracil H(5) and H(6) protons [2a], and the IR ν(C=O imide) stretching vibrations are shifted (about 60–120 cm^{-1}) towards lower frequencies. This means that the C=O bonds in uracils coordinated to the Fe(Cp)(CO)$_2$ moiety show increased single-bond character relative to those in N–H uracils, presumably as a result of d_π–p_π repulsion between the lone pair of electrons on nitrogen and a filled metal d_π orbital.

Unambiguous evidence for coordination of the Fe(Cp)(CO)$_2$ moiety to deprotonated N(3) is provided by the X-ray crystal structure of **2b**. A perspective view of this complex is shown in Fig. 1, together with the atomic numbering. Crystal data are listed in Table 3, final atomic coordinates in Table 4, and selected bond lengths, angles and torsion angles in Tables 5 and 6.

The coordination of the iron atom gives rise to a "three-legged piano-stool" configuration. According to Davies and coworkers [9], such complexes most often can be described in terms of a pseudo-octahedral arrangement of the ligands around the iron atom. The crucial structural features of pseudo-octahedral coordination are the three bond angles between M–(piano-leg) bonds close to 90° and the three angles between M–(piano-leg) bonds and the line M–Cp* (Cp* denotes the centroid of a cyclopentadienyl group) close to 125°. In **2b** these angles range from 92.1(3) to 94.3(2)° and from 120.9(4) to 124.1(3)° respectively. The geometry of the Fe(Cp)(CO)$_2$ moiety is similar to that observed in other related complexes. The cyclopentadienyl ring is essentially planar (within a 1σ range) and the Fe–Cp plane distance of 1.717(4) Å is only slightly longer than

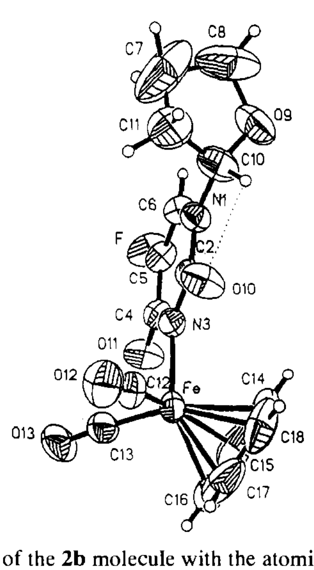


Fig. 1. View of the **2b** molecule with the atomic numbering.

Table 3
Crystal data and structure refinement details [a]

Crystal parameters	
Formula	$C_{15}H_{13}O_5N_2FFe$
Formula weight	376.12
Crystal system	Orthorhombic
Crystal color	Red
Crystal size (mm)	0.15×0.2×0.2
Space group	$P2_12_12_1$
a (Å)	6.298(1)
b (Å)	9.834(2)
c (Å)	24.518(5)
V (Å^3)	1518.5(5)
Z	4
D_c (Mg m^{-3})	1.645
F(000)	768
μ(Mo Kα) (mm^{-1})	1.03
T (K)	293
Transmission minimum; transmission maximum	0.553; 0.619
Data collection and refinement	
θ range for data collection	$1.66° < \theta < 27.56°$
Data collected (h, k, l)	$0 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 31$
Reflections collected	1986
Parameter of independent observed reflection ($F_0 \geqslant n\sigma(F_0)$)	1861 (n = 4)
Variation in standards	< 0.05
Refinement method	Full-matrix least-squares on F^2
Extinction coeficient	0.005(2)
Final R [b]	0.0421
Δ/σ(maximum)	0.02
$\Delta\rho_{max}$ (electrons Å^{-3})	0.64
N_o/N_v	8.31
Number of reference parameters	224
Goodness of fit [c]	1.086
Weighting scheme	$w^{-1} = \sigma^2(F_o) + (0.0857P)^2 + 1.00P$, where $P = (\max(F_0^2, 0) + 2F_c^2)/3$
Absolute structure Flack x parameter	−0.05(4)

[a] Details in common: Siemens P3 diffractometer, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).
[b] $R = \Sigma|F_o - F_c|/\Sigma F_o$.
[c] Goodness of fit in $[\Sigma w|F_0^2 - F_c^2|^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observation and N_v the number of variables.

Table 4
Atomic coordinates for Fe, F, N O, C and U_{eq}

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Fe	9377.5(10)	1060.2(6)	8227.3(2)	40(1)
F	13183(6)	1687(4)	10130(1)	68(1)
N(1)	12617(7)	4148(4)	9071(2)	40(1)
N(3)	11112(6)	2072(4)	8772(2)	46(1)
O(9)	12849(11)	6385(5)	9446(3)	97(2)
O(10)	11276(8)	3937(3)	8221(2)	64(1)
O(11)	11042(8)	270(4)	9362(2)	63(1)
O(12)	11926(8)	1799(6)	7282(2)	76(1)
O(13)	11647(9)	−1493(4)	8335(2)	81(2)
C(2)	11648(8)	3405(5)	8661(2)	44(1)
C(4)	11569(8)	1452(5)	9256(2)	48(1)
C(5)	12710(8)	2276(5)	9647(2)	47(1)
C(6)	13171(8)	3569(5)	9558(2)	42(1)
C(7)	16432(16)	6275(16)	9194(8)	163(7)
C(8)	14850(26)	7019(11)	9561(5)	139(5)
C(10)	13114(13)	5572(6)	8956(3)	64(2)
C(11)	15149(15)	5763(8)	8735(4)	94(3)
C(12)	10983(8)	1539(6)	7665(2)	49(1)
C(13)	10785(10)	−480(5)	8315(2)	54(1)
C(14)	6698(10)	2004(9)	8548(4)	81(2)
C(15)	6576(12)	672(11)	8654(4)	90(3)
C(16)	6563(13)	7(10)	8159(7)	128(5)
C(17)	6695(12)	981(17)	7764(3)	121(5)
C(18)	6752(12)	2246(10)	8008(4)	93(3)
Calculated coordinates of the center of C_5H_5 ring				
Cp*	6658(13)	1182(17)	8226(7)	

Table 5
Selected bond lengths (Å) and angles (°)

(a) *Fe coordination sphere*			
Bond lengths			
Fe–N(3)	1.991(4)	Fe–C(13)	1.768(5)
Fe–C(12)	1.774(5)	Fe–Cp*	1.717(4)
Bond angles			
C(12)–Fe–C(13)	92.1(3)	Fe–Cp* –N(3)	120.9(4)
C(12)–Fe–N(3)	94.3(2)	Fe–Cp* –C(12)	123.3(3)
C(13)–Fe–N(3)	94.1(2)	Fe–Cp* –C(13)	124.1(3)
C(2)–N(3)–Fe	118.4(3)	C(4)–N(3)–Fe	118.4(3)
(b) *Ftorafur group*			
Bond lengths			
N(3)–C(2)	1.381(6)	O(10)–C(2)	1.221(6)
N(3)–C(4)	1.366(6)	O(11)–C(4)	1.236(6)
N(1)–C(2)	1.386(6)	F–C(5)	1.352(5)
N(1)–C(6)	1.368(7)	C(7)–C(8)	1.53(2)
N(1)–C(10)	1.462(7)	C(7)–C(11)	1.47(2)
C(5)–C(6)	1.322(7)	C(8)–O(9)	1.43(1)
C(5)–C(4)	1.446(7)	O(9)–C(10)	1.45(1)
		C(10)–C(11)	1.40(1)
Bond angles			
C(4)–N(3)–C(2)	123.0(4)	C(11)–C(7)–C(8)	104.8(8)
N(3)–C(2)–N(1)	117.7(4)	O(9)–C(8)–C(7)	104.4(8)
C(6)–N(1)–C(2)	121.8(4)	C(8)–O(9)–C(10)	107.5(8)
C(5)–C(6)–N(1)	119.2(5)	C(11)–C(10)–O(9)	110.5(7)
C(4)–C(5)–C(6)	122.7(5)	C(10)–C(11)–C(7)	104.6(8)
N(3)–C(4)–C(5)	115.5(4)		

the reported average value of 1.71 Å [10]. The Ftorafur ion is η^1-*N* coordinated to the iron atom, with an Fe–N(3) bond of 1.991(4) Å. This bond is not perfectly coplanar with the N(3)–C(2) and N(3)–C(4) bonds. The distance of the Fe atom from the N(3)–C(2)–C(4) plane is 0.167(1) Å. The complexes Fe(Cp)(CO)$_2$L, where L is a nitrogen donor ligand, have not been much investigated. A literature search revealed only six structures of this type: two with linear ligands and four with cyclic ligands. The reported Fe–N distances are 1.979(7) Å [11], 1.970(7) Å [12], 1.98(3) Å [13] and 1.956(3) Å [5] for L = 1,2,3-triazole, benzimidazole, pyridine and phthalimide respectively, whereas the value for **2b** is 1.991(4) Å. The comparison of the bond lengths and angles in the Fe-coordinated Ftorafur anion with those found in the α and β forms of Ftorafur [14,15] is shown in Fig. 2. There is no significant change in the Ftorafur bond lengths upon coordination, but there are definite changes in the bond angles. Coordination results in considerable reduction in the C(2)–N(3)–C(4) angle and increases in the adjacent N(3)–C(2)–N(1) and N(3)–C(4)–C(5) angles. In α_A-, α_B- and β-Ftorafur molecules [14,15] the C(2)–N(3)–C(4) angle ranges

Table 6
The torsion angles of the tetrahydrofuranyl ring and of their connection with the uracil ring in the known structures of Ftorafur molecule (estimated standard deviations from 1 to 0.2°)

	Torsion angle (°)				
	α form		β form	Au complex	Fe complex (this work)
	A	B			
C(8)–O(9)–C(10)–C(11)	−14.1	−12.2	−8.5	−3.2	−5
O(9)–C(10)–C(11)–C(7)	−8.8	31.3	28.9	25.5	22
C(10)–C(7)–C(11)–C(8)	26.5	−36.9	−36.8	−36.1	−29
O(9)–C(7)–C(8)–C(11)	−35.6	30.6	32.6	35.3	26
C(10)–C(8)–O(9)–C(11)	31.8	−12.0	−15.6	−20.3	−13
C(6)–N(1)–C(10)–C(11)	−63.7	99.4	97.1	106.4	86.8
O(9)–N(1)–C(10)–C(6)	52.6	−17.3	−20.0	−12.2	−37.7
N(1)–C(10)–O(9)–C(11)	−135.5	107.9	111.3	116.7	121.1
N(1)–C(10)–C(11)–C(7)	108.1	−86.2	−89.0	−93.3	−102.6

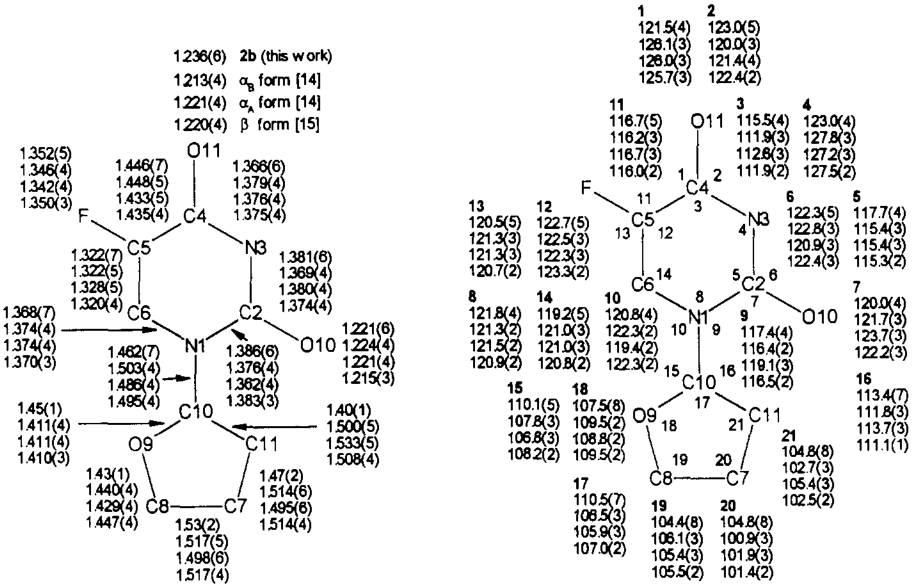


Fig. 2. Bond lengths (Å) and angles (°) in **2b** (this work) and in the α_B, α_A and β forms of Ftorafur.

from 127.2(3) to 127.8(2)°, with an average value of 127.5(2)°, and in **2b** the average is 123.0(4)°; the N(3)–C(2)–N(1) and N3–C4–C5 angles increase from average values of 115.4(3) and 112.1(2)° respectively in α- and β-Ftorafur molecules to 117.7(4) and 115.5(4)° respectively in **2b**.

Comparison of the three relevant angles with those found in the Au complex (121.3(23), 120.5(19) and 116.5(24) respectively [16], which confirm the observed tendency) is not significant because of the large estimated standard deviations in the data for the latter. The observed deformation of the considered bond angles is consistent with the expected structural changes in the uracil fragment brought about by the coordination [17–19]. The conformation of the the tetrahydrofuran ring in **2b** is significantly different from those in the α and β forms of Ftorafur and its gold(I) complex. Table 6 lists the torsion angles for this ring and its linkage with the uracil ring in the known structures of Ftorafur and its metal complexes. The dominant conformation of the five-membered ring is a C_2 half-chair configuration. It is observed as C_2(C(10)) in the α_A and C_2(O(9)) in the α_B and β forms of Ftorafur with asymmetry parameters [20] ΔC_2 of 5.3, 0.5 and 5.7° respectively. Only in the Au complex does this ring have an envelope C_s(C(7)) conformation with a ΔC_s(C(7)) value of 3.7°. In **2b** the tetrahydrofuran ring has a conformation intermediate between C_s(C(7)) and C_2(O(9)) with very similar asymmetry parameters, namely ΔC_s(C(7)) = 6.7 and ΔC_2(O(9)) = 6.3°. The degrees of puckering of this ring (as indicated by the average value of the intraring torsion angles $|\varphi|_{av}$) are similar (ranging from 23.4 to 24.6°) in all the known structures involving Ftorafur, except for the Fe complex. In **2b** the value of $|\varphi|_{av}$ is 19.0°. The mutual orientation of the tetrahydrofuran and uracil rings is determined by the intramolecular C–H · · · O bond. Fig. 3 shows the shortened intramolecular C–H · · · O distances in **2b** and in the α and β forms of Ftorafur [14,15]. According to Taylor and Kennard [21], a C–H group adjacent to a nitrogen atom is especially likely to form C–H · · · O hydrogen bonds, and this can be a significant factor in determining the minimum energy of organic molecules. The shortest C(10) · · · O(10) distance, 2.679(8) Å is observed for **2b** with an H(10) · · · O(10) contact distance of 2.30 Å and a C(10)–H(10) · · · O(10) angle of 102°. Similar but weaker intramolecular C–H · · · O bonds are observed in ftorafur itself. In the α_A form of this compound there is again a C(10)–H(10) · · · O(10) bond with the distinctly longer C(10) · · · O(10) contact of 2.776(5) Å. On the contrary in the α_B and β forms of Ftorafur, C(6)–H(6) · · · O(9) hydrogen bonds are observed. The interplane angle between the average planes of the tetrahydrofuranyl and uracil rings in α_A, α_B and β

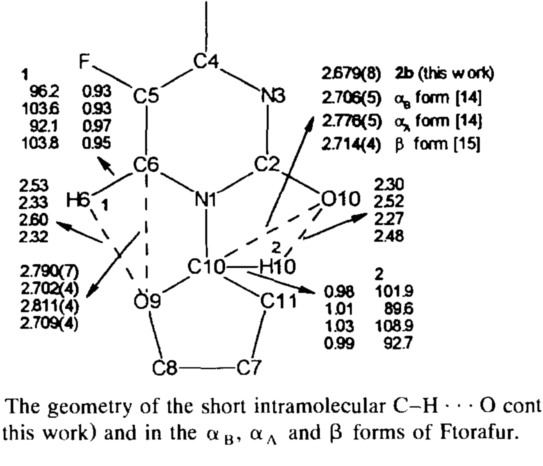
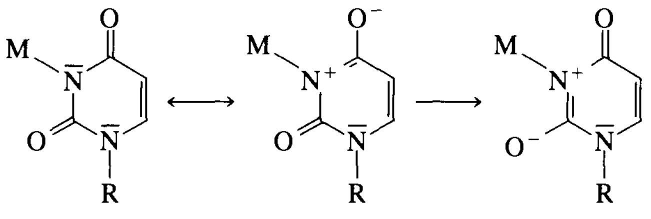


Fig. 3. The geometry of the short intramolecular C–H · · · O contacts in **2b** (this work) and in the α_B, α_A and β forms of Ftorafur.

forms of Ftorafur are 94.3(1), 82.3(1) and 100(1)° respectively, whereas in **2b** it is only 79.5(3)°.

The formation of the hydrogen bond between hydrogen at C(10) and O(10) in **2b** can be accounted for by assuming that there is a substantial negative charge on this oxygen atom, making it a more efficient hydrogen acceptor than the same atom in **1b**. This may be due to stabilization of the mesomeric forms such as **B** and **C** relative to **A** by d_π–p_π repulsion in the latter structure and a high polarity of the iron–nitrogen bond (Fe$^{\delta+}$–N$^{\delta-}$):



A **B** **C**

Unfortunately, the comparison of the C–N and C–O bonding distances in **2b** with those found for Ftorafur (Fig. 2) does not provide unambigous evidence for this suggestion, the observed bond length changes being smaller than 3σ (the average lengths of the C=O bonds are 1.220(4) Å and 1.228(6) Å for Ftorafur and **2b** respectively). The C=O(11) and C=O(10) distances in all the molecules considered are longer than the typical carbon–oxygen double bonds. The observed intraring C–N distances in **2b** and in Ftorafur indicate that there is uniform delocalization. (The average lengths of these bonds range from 1.373(4) to 1.374(4) Å in Ftorafur and from 1.366(6) to 1.386(6) Å in **2b**).

Replacement of hydrogen at N(3) in Ftorafur by the Fe(Cp)(CO)$_2$ group gives rise to a downfield shift (0.05 ppm) of the NMR signal from the proton at C(10), whereas the signals from all other protons in Ftorafur are shifted upfield. This suggests that the intramolecular hydrogen bond in **2b** may exist also in solution. Interestingly, the same phenomenon is observed in the case of 6-azauridine-2′,3′,5′-triacetate and **2c**.

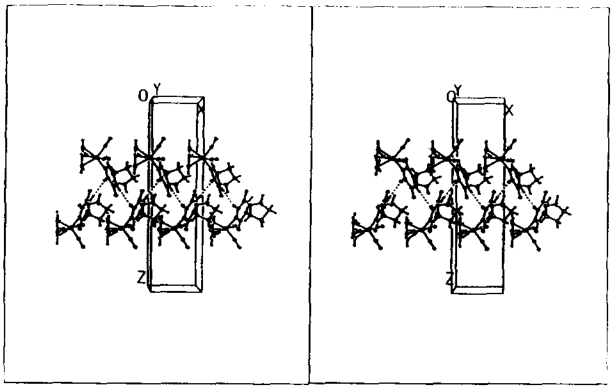
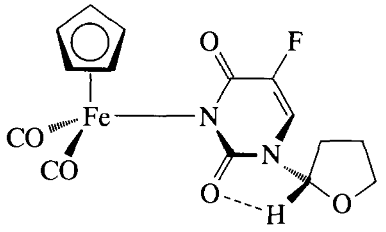
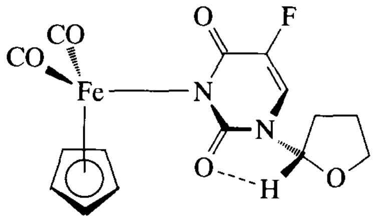


Fig. 4. Molecular packing.

The absence of symmetry of the deprotonated uracils makes their Fe(Cp)(CO)$_2$ complexes chiral if they adopt a conformation in which the uracil plane is orthogonal to the Fe–Cp*–N(3) plane. (This is roughly the case for **2b**, in which the dihedral angle between the planes is 86.5(3)°). Consequently, two enantiomers can be expected. If there is a free rotation around the Fe–N(3) bond, these enantiomers are interconverted (and are in fact conformers). As **2b** also contains a center of chirality at C(10), four stereoisomers (two diastereoisomers, each as a pair of enantiomers) are possible. Again, if there is free rotation around the Fe–N(3) bond, diastereoisomers having the same configuration at C(10) (e.g. **2b′** and **2b″**) interchange and should be considered as conformers:



(2b′)



(2b″)

The ^{1}H NMR spectrum of **2b** (no doubling of resonances at room temperature) confirms that either there is only one diastereoisomer present in solution or there is a free rotation around the Fe–N bond. In the solid state, the X-ray structure of **2b** is for the diastereoisomer in which both CO ligands and the oxygen atom of the tetrahydrofuran ring are on the opposite sides of the uracyl ring plane (as in **2b″**). Moreover, despite the fact that racemic Ftorafur was used in the synthesis of **2b**, the investigated crystal contained only molecules with one configuration at C(10) (S). Presumably, packing requirements favor crystallization of enantiomers as separate crystals. Unfortunately, the slow crystallization required for X-ray quality crystals is accompanied by extensive decomposition of **2b**, and we were not able to obtain further enantiomorphic crystals in order to separate them and to measure the optical activity of their solution.

The molecular packing in the unit cell of **2b** is shown in Fig. 4. The uracil rings parallel to the *x* axis are linked in the double chain by intermolecular hydrogen bonds O(11) ··· H(6)–C(6) with O(11)–C(6) and O(11)–H(6) distances of 3.403(8) and 2.51 Å, and an O(11) ··· H(6) –C(6) angle of 162°.

We plan to examine the antitumor activity of **2b**.

3. Experimental details

Proton NMR spectra were recorded on a Varian Gemini 200 BB spectrometer at 200 MHz with tetramethylsilane as internal reference. IR spectra were obtained on a Specord 75 IR spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Centre of Molecular and Macromolecular Studies (Łódź).

3.1. Materials

The uracils **1a–1c** were purchased from Aldrich. $Fe(Cp)(CO)_2I$ was prepared by the published procedure [22]. Benzene was distilled before use from sodium diphenylketyl and diisopropylamine from calcium hydride. All other solvents were of reagent grade and were used without purification. Kieselgel 60 (Merck; 230–400 mesh ASTM) was used for column chromatography, with chloroform as eluent.

*3.2. Preparation of **2a–2c***

A solution of $Fe(Cp)(CO)_2I$ (0.750 g, 2.46 mmol) and one of the uracils **1a–1c** (1 mmol) in benzene (10 cm^3) containing diisopropylamine (3 cm^3) was irradiated (visible light; 4 × 150 W tungsten lamps) for 2 h at 0°C under argon. The resulting yellow solid was filtered off and washed repeatedly with ether until the filtrate was colorless. Removal of solvent from the combined benzene and ether filtrates and chromatography of the residue afforded unchanged $Fe(Cp)(CO)_2I$ followed by yellow crystals of **2a–2c**. Analytical samples were prepared by crystallization from chloroform–heptane (**2a–2b**) or ether–pentane (**2c**).

3.3. Crystal structure analysis

Crystals of **2b** suitable for an X-ray study were grown from chloroform–heptane during 2 days. Crystal data and details of data collection and refinement are listed in Table 3. The intensities were corrected for Lorentz and polarization effects. An empirical correction was made for absorption [23] using a ψ scan around the diffraction vectors of eight selected reflections. The structure was solved by direct methods, and refined by the full-matrix least-squares method using the SHELXTL programs [24,25]. All non-hydrogen atoms were refined anisotropically. All H atoms were located in the difference map at $R = 0.06$ but, since their isotropic refinement was not successful, they were placed in calculated positions and refined isotropically by the "riding mode", except that the isotropic temperature factors of the H atoms bonded to C(7), C(8) and C(11) atoms were fixed at 0.08 Å^2. The absolute configuration of the molecule in the investigated crystal was determined by the Flack [26] method with a Flack parameter x of $-0.05(4)$.

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